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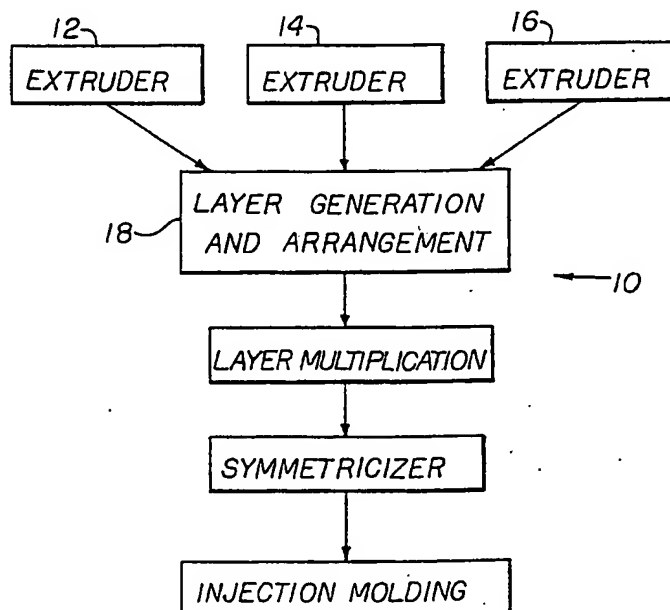
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b> B29C 43/20, 45/02, 45/16 B29C 49/04, 49/06, 49/22	<b>A1</b>	<b>(11) International Publication Number:</b> WO 91/09719 <b>(43) International Publication Date:</b> 11 July 1991 (11.07.91)
<b>(21) International Application Number:</b> PCT/US90/07327 <b>(22) International Filing Date:</b> 11 December 1990 (11.12.90) <b>(30) Priority data:</b> 456,718                      26 December 1989 (26.12.89) US <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). <b>(72) Inventors:</b> SCHRENK, Walter, J. ; 1307 Timber Drive, Midland, MI 48640 (US). SHASTRI, Ranganath, K. ; 3224 Fuller Drive, Midland, MI 48640 (US). ROEHRS, Herbert, C. ; 4528 South M-18, Beaverton, MI 48612 (US). AYRES, Ralph, E. ; 5501 Nurmi Drive, Midland, MI 48640 (US).		<b>(74) Agent:</b> MILLER, William, B.; The Dow Chemical Com- pany, P.O. Box 1967, Midland, MI 48640 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BB, BE (European patent), BG, CA, CH (European patent), DE (European patent), DK (European patent), ES (Euro- pean patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European pa- tent), JP, KR, LK, LU (European patent), MC, MG, MW, NL (European patent), NO, RO, SD, SE (Euro- pean patent), SU.  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>

**(54) Title:** PROCESSES AND APPARATUS FOR MAKING MULTILAYER PLASTIC ARTICLES

**(57) Abstract**

Processes and apparatus for making multilayer plastic articles, wherein the articles are comprised of a number of discrete and substantially continuous layers adjacent critical surfaces of the articles, which display a substantial uniformity of composition with respect to property-affecting constituent materials adjacent such surfaces, or which have discrete and substantially continuous layers of these materials within a selected layer order adjacent critical surfaces of the articles.

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PROCESSES AND APPARATUS FOR MAKING MULTILAYER PLASTIC  
ARTICLES

The present invention relates to multilayer plastic articles and to processes and apparatus for making such articles.

5       It has been appreciated previously that articles comprising overlapping layers of diverse thermoplastic materials could realize a combination of properties which could not be realized otherwise, except  
10       by the synthesis of an entirely new material or the use of a prohibitively expensive existing material. A number of processes and apparatus have accordingly been developed or suggested for making moldable, three-dimensional multilayer plastic articles of this type.

15       Exemplary of these known processes and apparatus are those disclosed in United States Patents No. 4,525,134 to McHenry et al., 3,339,240 to Corbett, 4,410,482 to Subramanian, and 3,716,612 to Schrenk et  
20       al, and in European Application 0278403 (Mitsubishi Gas Chemical Company Inc.).

Each of these known processes and apparatus, however, possess some limitation with respect to  
25       complexity, materials limitations, limitations on the

number or arrangement of layers, limitations on the shapes of articles which can be made thereby, and so forth. None of these known processes and methods, additionally, are disclosed or suggested to be suitable for use with multicavity injection molding or in the  
5 context of a multicavity injection molding process, or more particularly for multicavity injection molding wherein differing mold geometries are involved.

10 The processes and apparatus of the present invention are not so limited, however. The moldable articles of the present invention comprise discrete and substantially continuous layers of a plurality of diverse thermoplastic materials, and can be produced  
15 with a substantial uniformity of composition in a multicavity injection molding process, even where differing mold geometries are involved and where one of the materials is present only as a minor component (less than about 15 percent by volume). These layers may also  
20 be prearranged in a selected layer order, which selected layer order will be preserved in the molded article.

The novel and improved processes and apparatus for making such articles begin with the coextrusion of  
25 discrete, generally planar layers of first and second diverse thermoplastic materials in a first composite stream. In one set of processes and apparatus, the first composite stream is thereafter formed directly into a desired configuration with certain desirable qualities  
30 by some process other than thermoforming, such as by injection molding, injection blow molding, extrusion blow molding, displacement blow molding, compression molding, or transfer molding. In another group of processes and apparatus contemplated by the present invention, the first composite stream is manipulated to

form a second composite stream having an increased number of discrete, generally planar layers of the first and second materials compared to the first composite stream, and the layered second composite stream is then formed into a desired configuration, for example by one  
5 of the above-mentioned processes.

Fig. 1 is a schematic of an apparatus of the present invention for injection molding multilayer plastic articles.  
10

Fig. 2 is a schematic illustration of the formation of a second composite stream from a first composite stream.

Fig. 3 is an exploded view of an apparatus for forming a second composite stream from a first composite stream as schematically illustrated in Fig. 2.  
15

"Figures 4A and 4B are photomicrographs of cross-sections of cans molded from brown and white polypropylene, with the cross-sections being taken near the lip of a respective can and comparing the uniformity of layer thicknesses and evenness of layer distribution which may be achieved by using a commercial Ross  
20 interfacial surface generator (Fig. 4A) and the ISG of Fig. 3 (Fig. 4B).  
25

Figures 4C (Ross) and 4D (ISG of Fig. 3) make a similar comparison of cross-sections from the middle of a can.  
30

Figures 4E (Ross) and 4F (ISG of Fig. 3) compare cross-sections near the bottom of a can.

Fig. 5A schematically depicts an apparatus for reducing the exposure of layer edges of a layered stream.

Fig. 5B depicts the inlet side of the apparatus  
5 of Fig. 5A.

Fig. 5C depicts the outlet side of the apparatus of Fig. 5A.

Fig. 6A is a photomicrographic view of a  
10 section of a layered melt stream before passing through the apparatus of Fig.'s 5A-C.

Fig. 6B is a photomicrographic view of the  
15 section of Fig. 6A, after passing through the apparatus of Fig.'s 5A-C.

Fig. 7A is a photomicrograph in cross-section  
20 of an article produced by transfer molding a melt stream which is as depicted in Fig. 6A.

Fig. 7B is a photomicrograph in cross-section  
of an article produced by transfer molding a melt stream which is as depicted in Fig. 6B.

Fig. 8 is a depiction of the location of cross-  
25 sectional micrographs taken with respect to transfer molded parts in a simulation of multicavity injection molding.

Figures 9A-H presents the series of micrographs  
30 whose locations are noted in Fig. 8.

Figures 10A-C shows a transfer molding apparatus as used to demonstrate the present invention.

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Figures 11A and 11B are cross-sectional photomicrographs taken along orthogonal axes of an article of the present invention constructed as set forth in Example 2 below."

5 Referring now to Figures 1-11, and more particularly to Fig. 1, an apparatus 10 of the present invention is schematically illustrated. Extruders 12, 14 and 16 of Fig. 1 are sources of first, second and  
10 third diverse heat plastified thermoplastic materials, respectively. The depiction of only three extruders as in Fig. 1 does not negate the presence and use of perhaps additional or even fewer extruders or sources of thermoplastic materials, where other or fewer materials  
15 are sought to be incorporated into layers of a multilayer article to be formed. Additional materials and layers of materials may be required, for example, where two materials or two at least partially incompatible materials joined by a third compatibilizing  
20 material cannot by themselves impart the desired improvement in properties to the articles to be formed.

25

30



It should be noted parenthetically that the term "diverse" is intended to suggest only some measurable distinction between such "diverse" materials. This distinction may be of a chemical nature, a physical nature, or in the nature of a difference in color, appearance or optical effect. It is not necessary that one material be, for example, polyethylene while a second, "diverse" material is polypropylene. Nor is it necessary that the materials themselves comprise but a single identifiable species, so that a mixture of polyethylene and polypropylene could comprise a "thermoplastic resinous material" for purposes of this invention, and would be diverse from polyethylene or polypropylene individually.

Means for generating and controllably or non-randomly arranging layers of the first, second and third materials in a first composite stream is schematically depicted in Fig. 1 and comprises in a preferred embodiment a coextrusion feedblock apparatus 18. A preferred coextrusion feedblock apparatus for generating and arranging layers of the first, second and third materials in a first composite stream is as disclosed in United States Patent No. 3,557,265 to Chisholm et al. or as disclosed in United States Patent No. 3,884,606 to Schrenk et al.

The present invention relies upon the arrangement of the extruders and the feedblock apparatus to control the thicknesses, distribution, and arrangement of layers of the various materials to be included in the first composite stream. In this way, it is a relatively simple matter in the context of the teachings of the coextrusion art:

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1) to order the layers of the first, second and third materials, for example, within a first composite stream so that the third material may be initially advantageously placed;

5                   2) to distribute the materials substantially evenly in the composite stream so that the distribution of the layers in the finished article will be relatively even also and the article will display a substantial  
10                   uniformity of composition with respect to at least the layers of property-affecting materials adjacent a critical surface of the article; and/or,

                  3) to select a layer thickness for layers of each of the various materials so that subsequent  
15                   manipulations of the emerging composite stream do not cause the layers of the various materials in the ultimately desired configuration to depart from a substantially continuous nature.

20                   By "substantially continuous," it is meant only that the individual layers have significantly more of the character of a continuous layer extending throughout and around the walls or boundaries of an article, and  
25                   more particularly adjacent a critical surface of the article, than any partial lamellae which would be created in accordance with or suggested by the teachings of the prior art.

30                   A "critical surface" refers to a surface of the article which will be subject to various stresses or wherein the properties which are sought to be enhanced by a lamellar construction will be desired. Where the object is to enhance barrier properties in an article with respect to a particular gas or solvent, for

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example, a critical surface would correspond to any surface which is expected to contact that gas or solvent and to form a barrier to permeation of the gas or solvent therethrough.

5           We consider that no more than about 10 percent of these layers of the property-affecting materials of interest should have an interfacial surface area to unit thickness ratio of less than 10:1 to realize the  
10           benefits and advantages of our invention, although preferably and typically the dimensions and thicknesses of layers created by the processes of our invention will be such that multilayer articles produced thereby have properties and a cross-sectional microscopic appearance  
15           approaching those of a thin, flat coextruded sheet. Thus, the interfacial surface area to unit thickness ratio for layers of the property-affecting materials of interest adjacent a critical surface of an article will preferably be at least 100:1, and most preferably at  
20           least 1000:1.

          The referenced interfacial surface area to unit thickness ratio is calculated by resolving a layer into an element of length  $l$  and of width  $w$ , with a unitary  
25           thickness. Thus, where a layer is observed to approximate in interfacial surface area a rectangle of length  $l_1$  and width  $w_1$ , and is observed to have an average thickness  $t$ ,  $l=l_1/t$  and  $w=w_1/t$  approximately. The amounts  $l$  and  $w$  can be thought of as expressing the  
30           degree of extensiveness of a given layer in a direction compared to other layers of a like thickness. The interfacial surface area to unit thickness ratio of a given layer would be represented by the product  
 $lw=(l_1/t)(w_1/t)=l_1w_1/t^2$ .

In considering how this ratio applies to describe our layers, one may refer to the cross-sectional photomicrographs of Fig. 11A. These photomicrographs depict the cross-sections of a specimen from an article molded as described in Example 2 below.

5 The specimen was cut to expose cross-sections in the direction of flow during mold-fill and in a direction perpendicular thereto. The thickest layer which is clearly visible in Fig. 11B can safely be assumed to encompass an interfacial surface area at least equal to

10 the product of the width of photomicrograph A and the distance from the right edge of B to where the white material appears in the midst of the layer, or at least equal to about  $3.5 \times 1.5 = 5.25$  square inches ( $33.87$

15  $\text{cm}^2$ ) on the scale of the photomicrographs. On the same scale, the thickness of the layer appears not to exceed about .2 inches (.5 cm) on the average, so that the interfacial surface area to unit thickness ratio for this layer appears to be at least about

20  $5.25/(.2) = 131.25$ .

Further, one can discern a number of layers immediately above the layer just discussed which appear to be fully continuous over the widths of both

25 photomicrographs, and yet have a thickness substantially less than that of the thickest layer so that the interfacial surface area to unit thickness ratio for these substantially parallel layers should be much greater than the about 131.25 ratio seen for the

30 thickest layer. For example, the layer immediately above the thickest layer would appear to have an interfacial surface area of at least about  $3.5 \times 3.5 = 12.25$  square inches ( $79.0 \text{ cm}^2$ ), and a thickness not exceeding .05 inches ( $0.127 \text{ cm}$ ). The ratio for this layer would then

appear to be on the order of at least  $(3.5 \times 3.5) / .052 = (11w_1) / t_2 = 4900$ .

Given that none of the layers in Fig. 11 exhibit large fluctuations in thickness, it appears likely that the layer above the thickest layer extends continuously for a still greater distance in both directions implicated in photomicrographs A and B, without dramatic corresponding increases in thickness such as would have the effect of decreasing the overall surface area to thickness ratio of the layer. Rather, the photomicrographs suggest that the full extent of the layer as seen on the scale of the photomicrographs may be significantly greater than 12.25 square inches (79.0 cm<sup>2</sup>) while the average thickness of the layer would be the same or less than the 0.05 inches (0.127) cm) used above, so that the layer were it to be measured in full would have an interfacial surface area to unit thickness ratio correspondingly greater than even 4900.

Also by way of definition, a "substantial uniformity of composition" as used herein refers to the deviation of the local composition ratio within a wall of the molded article from the average composition ratio of the article as a whole, the latter ratio being determined by the ratio of feed rates of individual polymer components to the processes of the present invention. The local composition ratio refers to the composition ratio of a specimen from adjacent a critical surface of the molded article, the specimen being derived from within the composite stream in its desired configuration and having dimensions of at least the local thickness of the molded article in all directions.

A "substantial uniformity of composition" exists where local composition ratios along a critical surface of the article do not vary by more than 20 percent, and preferably no more than 10 percent, from the average composition ratio. In general terms, this  
5 substantial uniformity of composition is important in achieving a uniformity of properties along a critical surface of the article in the desired configuration.

Returning to a discussion of the coextrusion  
10 feedblock apparatus 18 illustrated schematically in Figure 1, it will usually be desirable to employ a 2, 3, 4 or 5-layer feedblock apparatus where only the first and second materials are used, so as to create for  
15 example with the 5-layer apparatus an ABABA-type layer structure in the first composite stream, or where first, second and third materials are used, creating an ABCBA-type structure for instance. Where such a 2,3,4 or 5-layer feedblock apparatus is used, it is thought that a  
20 feedblock such as is disclosed in United States Patent No. 3,577,265 to Chisholm et al. should be satisfactory, and a number of total layers of the first and second, or of the first, second and third materials in excess of  
25 the 2, 3, 4 or 5 respectively created thereby may be created by employing means for manipulating the first composite stream from coextrusion feedblock apparatus 18 to form a second composite stream which has an increased number of layers of the first and second, or of the  
30 first, second and third materials compared to the first composite stream. This manipulation is characterized in Figure 1 as "Layer Multiplication."

This means for manipulating the first composite stream to form a second composite stream preferably includes means for dividing the first composite stream

to form a plurality of substreams which collectively  
comprise an increased number of layers of the first and  
second, or of the first, second and third materials  
compared with the first composite stream, and means for  
combining the substreams to form the second composite  
5 stream. The formation of the second composite stream  
from the first composite stream and a preferred  
apparatus for accomplishing this formation are  
schematically shown in Figures 1 and 2, and shown in  
10 more detail in Fig. 3.

Referring now to Fig. 2 specifically, a  
schematic of the creation of additional layers of the  
first and second materials of the first composite stream  
15 for the second composite stream is illustrated, and  
shows that a melt stream comprised of layers 19a and  
19b, respectively, of the first and second materials in  
an ABA-type construction is divided in a plane which is  
generally perpendicular to the layers of the melt  
20 stream, then flattened and recombined by means for  
stacking the substreams. "Stacking" the substreams in  
this manner refers to the recombination of the sub-  
streams in a direction which is generally perpendicular  
to the layers of the substreams, such that the combined  
25 layers of the substreams are substantially parallel to  
one another.

An apparatus for dividing the first composite  
stream to form a plurality of substreams and to  
30 recombine these substreams to form a second composite  
stream by stacking the substreams is shown in Fig. 3.  
In Fig. 3 it can be seen that, at the entrance 20 of the  
interfacial surface generator (ISG) depicted in Fig. 3 a  
first composite stream represented by the arrow 22 is  
divided by a blade or thin wall section 24 which is

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generally perpendicularly oriented with respect to the layers of the first composite stream.

5 A substream 26 of the first composite stream ascends a generally rectangular-shaped, sloping passageway 28 to the left of blade 24, while a second substream 30 of the first composite stream descends a passageway 32 to the right of blade 24 which is similar in shape to the passageway 28 but which slopes downward.

10 Substreams 26 and 30 are then essentially stacked by passageways 34 and 36, with passageway 34 forcing substream 26 back to the right and passageway 36 forcing substream 30 to the left. The layers are kept from mixing during these lateral movements by a blade or  
15 thin wall section 38 which is oriented generally parallel to the layers of the substreams 26 and 30.

20 Substream 26 is then flattened and forced downward in a passageway 40 while substream 30 is flattened and forced upward in a passageway 42, the substreams 26 and 30 again being prevented from mixing by a thin wall section 44. The substreams 26 and 30 are then allowed to recombine to form a second composite  
25 stream which has a greater number of layers of the first and second materials than the first composite stream.

30 By using an apparatus such as is depicted in Figures 2 and 3, or by using other conventional ISG's such as sold by Charles Ross & Son Company, P. O. Box 2200, Hauppauge, N.Y., USA 11787 or as described in United States Patent No. 3,195,865, a great many layers of the various materials can be created by a sort of layer multiplication process.



An equivalent number of layers might be formed merely by using a larger coextrusion feedblock apparatus, such as disclosed in United States Patent No. 3,884,606 to Schrenk et al., and the coextrusion feedblock apparatus of that patent is preferred over  
5 more conventional feedblock apparatus employing a linear feedblock where a fairly large number of layers is to be generated without the use of the sort of apparatus depicted in Figures 2 and 3.

10 Under such circumstances, an apparatus as disclosed in United States Patent No. 3,884,606 should be less likely to contribute to a significant proportion of the layers at the edges of the first or second  
15 composite stream becoming discontinuous on forming the stream into a desired configuration.

As a rule, though, as compared to the use of a coextrusion feedblock apparatus alone, a standard 2, 3,  
20 4 or 5-layer coextrusion feedblock apparatus is preferably used in combination with one or more ISG's as described above. As for selecting the type or types of ISG's for a particular application, it should be observed that the various known ISG's which could be  
25 used will generally distort the composite stream from the coextrusion feedblock apparatus to different degrees.

The ISG of Figures 2 and 3 generally produces  
30 less distortion of the nonrandomly arranged composite stream emerging from the coextrusion feedblock apparatus, for example, and a greater uniformity in layer thicknesses within the second composite stream and in an injection molded article having a desired configuration than do the commercially available four

channel Ross elements with respect to layers of a given material. This difference is particularly illustrated in Figure 4A-F, which shows a series of comparative photomicrographs of cross-sections of a wall of a can which has been injection molded from layers of brown and white polypropylene, using ISG's of the type shown in Fig.3 and the Ross ISG's.

A lesser distortion of the first composite stream in the creation of the second composite stream should typically mean a lesser departure from the properties and characteristics desirably imparted to the first composite stream in the coextrusion feedblock apparatus 18, and a greater likelihood of those characteristics being transferred through to the finished article with fewer variables being involved in trying to achieve a desired configuration of that article having those properties.

Determining when one might desire to use a coextrusion feedblock apparatus only or in an ISG/feedblock combination with a particular combination of ISG's depends on a number of considerations, including for example:

1) whether the equipment is to be dedicated to a particular application for a sufficient length of time that the decreased flexibility involved in using a feedblock apparatus alone is not counterproductive in an overall sense;

2) whether the application is of such a demanding nature that the distortion involved in the manipulation of layers in the ISG's that would be required is of a sufficient nature that the generally

increased fabrication costs associated with a complex feedback apparatus is offset;

3) the availability of space and equipment, and specifically as to the latter, the availability of an  
5 appropriate feedback apparatus;

4) the degree of distortion introduced with each ISG, within the limits imposed on the length of the ISG's by degradation and space concerns; and  
10

5) whether a degree of degradation may be tolerated with respect to certain materials in the interests of lesser layer distortion through the ISG's.

The significance of greater layer uniformity  
15 being transferred through to the finished article by the careful selection of appropriate layer generation, arrangement and/or multiplication means lies in part, it is believed, in the optimization of those properties  
20 which are enhanced by a lamellar construction.

It has generally been noted that for a given system of diverse thermoplastic resinous materials in a given mold geometry, an optimum mix of properties may  
25 correspond roughly to a given number or range of numbers of layers of such property-affecting materials. Where this number of layers is large, or the wall thickness locally small adjacent a critical surface of the article, it may be difficult to achieve this optimal  
30 blend of properties throughout an article.

Further, it is generally true that all other things being equal, the larger the number of layers across a cross-section of the wall of an article, the greater the improvement in those properties which are

enhanced by a lamellar construction, so long as the layers are substantially co-continuous across that cross-section of the article.

A significant variation in the layer  
5 thicknesses of a given property-affecting material across such a cross-section can be viewed as effectively reducing the number of layers of such a material as some layers approach a discontinuous nature, and while the effect of the difference in the amount of distortion  
10 involved in using one type of ISG as opposed to another might be small in one application, for other systems the effect might be sufficiently significant to warrant a preference for one type or one particular combination of ISG's.  
15

Whether the desired number of layers is created in a second composite stream by the combination of a coextrusion feedblock apparatus and an ISG or a series  
20 of ISG's, or in a first composite stream merely by a coextrusion feedblock apparatus, a resulting layered melt stream is molded into a desired configuration by means for accomplishing this function, or the stream may first be passed through what has for present purposes  
25 been termed a "symmetricizer".

A "symmetricizer" is a device which has been developed for reducing the number and extent of exposed layer edges in a layered melt stream including diverse  
30 thermoplastic resinous materials prior to forming the stream into a desired configuration by injection molding, compression molding, transfer molding, injection blow molding, displacement blow molding or extrusion blow molding, and for correspondingly reducing

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the exposure of layer edges in that desired configuration of an article.

5 A symmetricizer might appropriately be employed where the properties which are sought to be enhanced by a lamellar construction could be significantly adversely affected by the exposure of a number of layer edges at a surface of the finished article to external influences, and where because of the mold geometry, method of forming the article, the materials used, etc., such exposure is likely to occur. One example of such a situation might be where a saponified ethylene-vinyl acetate copolymer is being used to provide an oxygen barrier to an article produced in accordance with the present invention, where upon exposure to moisture in the article's environment a loss in barrier and mechanical properties can be expected.

20 In general the symmetricizer is designed to reduce the exposure of layer edges in a layered melt stream by dividing the stream into two or more substreams having layers of thermoplastic materials, and then combining these substreams such that a majority of the layers of one of the substreams are generally angularly oriented with respect to a majority of the layers of a second substream.

30 What is generally intended in the operation of the symmetricizer device of this invention is first, to dispose some of those layer edges which would otherwise initially come into contact with the walls of a mold at a perpendicular angle and freeze in such an orientation so that they initially contact the walls, if at all, at a significantly greater or lesser angle. Secondly, it is thought that placing the majority of the layers of

one of the substreams at an angle with respect to the majority of the layers of a second substream will create a tendency of the layer edges to enfold one another.

5 In the enfolded structures, the greater portion of layers of the first, second and third materials will preferably lie generally parallel to a critical surface, but with the layer edges of sensitive layers being interwoven and overlapping rather than intersecting a critical surface of the article.

10 Some degree of layer distortion is occasioned by this manipulation of the stream to be molded or otherwise formed into a desired configuration. The effects of this layer distortion are a cost associated with a reduction of exposed layer edges in the article, and it is expected that this cost will need to be considered in determining whether the use of a symmetricizer may be appropriate for a given application.

20 In multicavity injection molding it may not be necessary to employ an apparatus for reducing the exposure of layer edges where the use of the article and the materials used in constructing the article might otherwise suggest the advisability of such an apparatus, in that the flow of the layered stream through runners and gates will usually sufficiently randomize the layers of the stream to reduce the number and/or extent of exposed layer edges in both the layered stream and the finished article. Nevertheless, even in multicavity injection molding a symmetricizer may still be of some benefit in terms of the properties of articles produced thereby, and the desirability of employing a symmetricizer in any particular set of circumstances

might more suitably be judged on a case by case basis.

A preferred symmetricizer is shown in Figures 5A-C , and comprises a plurality of inlet ports 46 and a plurality of outlet ports 48, the outlet ports 48 being generally divided into central outlet ports 48a and peripheral outlet ports 48b. Inlet ports 46 are generally rectangular in shape, and preferably have a long dimension which is parallel to the layers of first, second and third materials of the first or second composite stream which are received therein. The internal channels 50 of the symmetricizer which correspond to inlet ports 46 and outlet ports 48 are preferably of a constant rectangular configuration which matches that of corresponding inlet ports 46 and outlet ports 48, and preferably provide an incrementally consistent change of orientation from an inlet port 46 to an outlet port 48, as suggested in Fig. 5A. As shown, outlet ports 48a associated with substreams of the first or second composite stream passing therethrough are oriented substantially at a 90° angle with respect to one another, as are outlet ports 48b.

An illustration of the transformation worked by the symmetricizer of Fig. 5A-C may be seen in Fig. 6A and 6B, which depicts cross-sections of a layered melt stream of brown and white polypropylene prior to and following passage through a symmetricizer configured as in Fig. 5. An indication of how the reduction in exposed layer edges accomplished by the symmetricizer can translate through the formation step to a finished article can be seen in Fig. 7A and 7B, which depicts photomicrographs of cross-sections of the walls of cans injection molded from the same brown and white polypropylene with and without the

symmetricizer. As may be seen from Figure 7A and 7B, the symmetricizer appears to have reduced at least the extent of layer edges which are perpendicular to a surface of the can, if not the number of such edges.

5 Referring back to Fig. 1, it can be seen that the first or second composite stream is thereafter molded into a desired configuration by a process other than thermoforming, such as by the preferred injection  
10 molding process or by compression molding, transfer molding, injection blow molding, displacement blow molding or extrusion blow molding.

The preferred manner of forming a first or second composite stream of the present invention into a  
15 desired configuration would, as previously suggested, involve some sort of injection molding. Coextrusion, though, has generally been developed as a continuous process, while injection molding is an intermittent  
20 process. One possible way in which the invention could be practiced with both processing methods integrated therein would use accumulators and valves to direct flow to one accumulator during the molding cycle of another.

25 Another possible way would be to use reciprocating screw injection of each of the first and second or first, second and third materials through the coextrusion feedblock apparatus, so that intermittent flow for injection molding is established before and  
30 during layer generation and arrangement into a composite melt stream, rather than afterwards.

A particularly preferred manner of forming a composite stream into a desired configuration involves multicavity injection molding. Previously, although it



had been demonstrated in United States Patent No. 3,716,612 that a lamellar construction could be transferred from a layered melt stream into a finished article after injection molding, it was not known whether such a lamellar construction could be maintained  
5 throughout the full extent of a multicavity mold where one of the layered components was present as a minor phase ( at less than about 15 percent by volume, for example). By the present invention, a lamellar  
10 construction can be maintained throughout the extent of a multicavity mold for even minor components within a lamellar melt stream.

Examining the operation of the apparatus  
15 described above in performing the processes of the present invention for making moldable multilayer plastic articles, one potential application would be in the making of plastic containers for carbonated beverages. Such containers have in the past been made of  
20 polyethylene terephthalate (PET), which forms a fairly good barrier to the loss of carbon dioxide from the beverage. In an effort to lengthen the shelf life of these beverage containers, especially for smaller such  
25 containers, one might wish to create a multilayer structure incorporating layers of PET and of a resin with a better barrier to CO<sub>2</sub>, such as an ethylene vinyl alcohol (EVOH).

In considering how one might achieve the  
30 benefits of the present invention with a PET/EVOH system as the first and second diverse thermoplastic materials, one approach that is presently foreseen would first match the viscosities of the PET and EVOH over a range of nondegradative temperatures within the general limits suggested by the coextrusion art, given the sensitivity

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of the system to discontinuities in layers and similar such considerations. For purposes of the present invention, generally materials having viscosities that differ by no greater than a factor of five can be appropriately used together in the present invention,  
5 and even greater viscosity mismatches might be tolerated, although the upper limits on this are not presently known.

The next step would be to consider whether PET  
10 and EVOH are sufficiently self-adhering to possess adequate structural integrity for a carbonated beverage container. If not, a third, compatibilizing material needs to be selected to adhere layers of the PET and  
15 EVOH together in the finished article.

A variety of compatibilizing materials are known, and may be advertised as adhering to both PET and EVOH, or may be known to adhere to both. Of those  
20 materials which emerge as potential candidates for use as the third material, one would select materials for further evaluation which could be matched to the PET and EVOH rheologically within the nondegradative temperature range established earlier, and which would not  
25 themselves degrade at the temperatures of interest.

The candidates could then be coextruded with the PET and EVOH, and peel tests conducted of the resulting structure to determine which of the candidate  
30 materials provided adequate adhesion and the amounts of such materials necessary to provide such adhesion. Taking into account such things as the materials cost associated with providing an adequate degree of adhesion

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and the availability of the material, a selection would then be made of the third material to be used.

5 The first, second, and third materials would then be melt coextruded with proper temperature controls on the source extruders to match the rheologies of the various materials, and with the second and third materials generally being used in the minimum amounts thought necessary to achieve a desired barrier, since the second and third materials will typically be more  
10 expensive than the first material whose purpose will normally be primarily of a structural nature. In this regard, it has been found that the second material can typically comprise less than about 10 percent by volume of the first composite stream without the layers of this  
15 material becoming discontinuous to an unacceptable degree when employed in a process and apparatus of the present invention.

20 One or more ISG's or a different feedback may then be employed, as discussed earlier, to increase the number of layers. Testing of the articles produced by the process for various numbers of ISG's should establish whether the desired barrier can be achieved  
25 for the materials and levels of materials employed. It should be noted that the ISG's used will generally be controlled as to temperature as well to ensure that throughout the process the rheologies of the various materials remain properly matched without degradation  
30 having occurred with respect to one or more of the constituent materials of the melt stream.

This degradation will be a function of the temperatures experienced within the process as well as of the time in which the materials are exposed to these

temperatures. Thus, the number of ISG's of a given length which can be employed may be limited, or the length of a given number of ISG's limited. We have found for the ISG's shown in Figures 2 and 3 that longer  
5 incoming layered melt stream and a greater uniformity of the outgoing stream through the thickness of the stream. This greater uniformity through the thickness of the stream is desirable in lessening the likelihood of  
10 unacceptable layer distortions and discontinuities in the finished article. It would therefore be desirable to use longer ISG's in the creation of the composite stream to be formed into the desired configuration, unless degradation of one or more of the materials in  
15 the melt stream is a problem. Other considerations may limit the length of the ISG's used for a given resin system and application, such as space limitations, for example, but degradation is of particular concern for most such systems and applications.

20 The foregoing illustrates one possible approach to applying the processes and apparatus of the present invention, although other approaches are believed possible and should be apparent to persons of ordinary  
25 skill in the art in view of the discussion above and of the examples which follow.

30 It may be that the only properties which are sought to be enhanced by a lamellar construction of an article are those relating to the appearance of the article. The teachings of this disclosure and specifically the apparatus taught herein may be adapted to this use as well, and this use is considered encompassed within the scope of the present invention.

The processes of the present invention and apparatus for performing the processes, and the articles which result therefrom are perhaps best further illustrated by the following examples.

5    Example 1

          In this example, a melt stream having a total of 129 alternating layers of brown and white pigmented polypropylene was created by extruding the brown and  
10   white polypropylene material through a three layer coextrusion feedblock apparatus, then feeding the resulting first composite stream through three of the four-channel Ross static mixers in series.

15           Extrusion rates within the apparatus of the present invention are in general calculated from the desired composition ratio in the molded part. Volumetric screw feeders were used in this and  
20   subsequent examples to meter pellets of the second and of the third compatibilizing material, if present, into 1 1/4 inch single screw 24:1 L:D extruders, with the extruder screw speeds set to maintain a starve-feed condition. The screw speed of the 1 3/4 inch single  
25   screw 24:1 L:D extruder used for the first material was then adjusted in this and other examples to obtain the desired total rate, which is determined by weight measurements with all of the extruders running.

30           A selection of polymer grades and an adjustment of individual melt temperatures to ensure a viscosity mismatch of a factor of no greater than 5 was undertaken in some of the other examples to obtain an acceptably uniform distribution of layers in the melt stream cross-section, as a severe mismatch in polymer viscosities can

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cause higher viscosity materials to channel through the center of the melt stream, resulting in edge-to-edge layer non-uniformity and local cross-sectional variation of composition ratio. Because the brown and white polypropylene used in this example had identical rheologies, however, these adjustments were not required for this particular example.

Ten ounce cans were transfer molded in a molding machine from a melt stream constructed as described above, with some cans being made after having had the melt stream pass through a symmetricizer as previously described. A layered "gob" was hand cut from the melt stream emerging from an ISG or from a symmetricizer and was manually deposited into the cold can mold shown in Figures 10A-C. Cans produced by the apparatus by bringing piston X and mold core Y together in the manner suggested by Figures 10A-C were studied by optical microscopy of specimens cut parallel and perpendicular to the flow direction of the material being molded, to verify the retention of the lamellar morphology of the melt stream and to ascertain the continuity or lack of continuity of the lamellae in the articles.

Substantially continuous layers were observed in all portions of the cans, and insofar as could be discerned by optical microscopy, cans formed after the addition of other ISG's to the series also possessed substantially continuous lamellae.

Fountain flow during mold fill was seen to have caused some layers to deform, stretch and fold over as materials diverted from the center of the mold channel to the mold wall, so that the number of layers in a

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cross-section was apparently increased and the orientation of layers relative to the inner or outer surfaces of the can varied along the sidewall's length. The apparent thickness of some of the layers shown in the accompanying photomicrographs may be somewhat  
5 deceiving, then, in that some of the layers must have been cut on a diagonal. This stretching and folding over did not appreciably affect the continuity of layers within the article, though.

10           Considering the photomicrographs of Fig. 7A and 7B, representative can sidewall cross-sections are shown which demonstrate the effect of the use of a symmetri-  
15 cizer. Layer edges without the symmetricizer solidified to a depth of approximately 20 percent of the wall thickness from both surfaces before the layers became substantially parallel to the surfaces.

20           In contrast, cans molded from a melt stream proceeding from a symmetricizer exhibited fewer layer edges at the inner and outer surfaces and layers were essentially substantially parallel to mold surfaces throughout the sidewalls of the container, as seen in Fig. 7A and 7B.

25           It should be noted for future examples using the can mold and transfer molding apparatus described above and shown in Fig. 10A-C that some difficulties were experienced with regard to the bottoms of cans  
30 produced by the apparatus. Layer patterns were generated in the can bottoms which were not matched by patterns created in the sidewalls of the cans, and such patterns are believed to be due to a number of factors peculiar to this transfer molding apparatus and process.

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When the "gob" is first dropped into the mold cavity some solidification occurs, freezing relatively thick layers at the surface. With the mold closed and the piston forcing the charge into the can's sidewalls, solidification continues at the piston face and on the  
5 mold core while the molten core materials fill the sidewalls. With dissimilar polymers, delamination can occur, and is observed to occur as the bottom is compressed in the last stage of molding, when much of  
10 the material comprising the bottom has already solidified. Injection molding through a gated mold cavity will substantially avoid these distortions.

Thus, while transfer molding has initially been  
15 used to simulate as nearly as possible actual simple injection molding in the absence of a suitable injection molding machine, the difficulties experienced with the can bottoms just described makes these transfer molded cans as a whole somewhat inferior with respect to cans  
20 which could be expected from actual injection molding, while such cans as were made are nevertheless sufficient to demonstrate the operability of the present invention. To obtain a better representation or approximation of  
25 the multilayer articles which would be produced by such actual injection molding, property evaluation with respect to the cans of this and other examples has been limited to the sidewalls thereof whenever possible.

### 30 Example 2

In this example, the same brown and white polypropylene was used with a coextrusion feedblock apparatus alone to create a first composite stream having 233 layers, which was then transfer molded as in Example 1. No symmetricizer was employed. Specimens



which were cut from throughout the sidewalls of the resulting cans, both parallel and perpendicular to the flow direction of the material being molded, showed substantially co-continuous lamellae also. Representative photomicrographs are provided in Figure 11A and 11B, and show the lamellae for a given specimen in the direction of flow and in a direction perpendicular to the flow of materials during mold-fill.

### Example 3

In this example, the same apparatus was employed as in Example 1, except that the can mold of Figure 10A-C was replaced by the multicavity test specimen tooling of Fig. 8, and that the three Ross ISG's of Example 1 were replaced by six ISG's of the variety shown in Fig. 3. The four cavity test specimen mold was selected to provide standard ASTM test specimens for purposes of testing mechanical properties and to more closely simulate conventional injection molding, since in the test specimen mold a lamellar melt stream would flow through standard runners and gates and to four mold cavities of differing geometries.

The same brown and white polypropylene materials used in Example 1 were formed into a 129 layer melt stream, and the melt stream molded into the four test parts. Optical microscopy of cross-sections taken in the places indicated in Fig. 8 resulted in the photomicrographs shown in Fig. 9A-H. Substantially continuous lamellae were observed throughout, and a substantially uniform composition appeared to have prevailed throughout all cavities irrespective of runner length and cavity flow length.

Example 4

This example explores the effects of using an ISG of the type shown in Fig. 3 versus a commercially available ISG in an otherwise identical process. Cans were made from the brown and white pigmented polypropylene materials of Example 1 in an apparatus constructed as in Example 1 and using in some runs three of the Ross ISG's and in other runs six of the ISG's shown in Fig. 3. Photomicrographs shown in Fig. 4A-F demonstrate clearly that the ISG's of Fig. 3 produce a significantly better uniformity of layer distribution than do the Ross ISG's, as has been previously suggested.

15 Example 5

Multilayer cans were molded from a second composite stream in two wall thicknesses, 32 and 42 mils, and in the can molding apparatus of Fig. 10A-C. A high density polyethylene was used as the first material and possessed a melt index of 8 grams per 10 minutes and a density at 25°C of 0.954 grams per cubic centimeter. The second material comprised an ethylene vinyl alcohol copolymer having a 29 mole percent ethylene content, a melt flow rate of 8 grams per 10 minutes, and a density of 1.21 grams per cubic centimeter at 25°C, such a copolymer being commercially available under the mark Soarnol D™ from Nippon Gohsei.

30 Because the HDPE and EVOH do not adhere to one another well, an anhydride-modified, linear low density polyethylene-based Plexar 2581™ adhesive resin produced by Quantum Chemical Company was selected as the third

material for adhering layers of the EVOH and HDPE together.

Each of the components was fed to an extruder as in Example 1, and combined in a five layer feedblock in an ABCBA-type layer order having layers of high density polyethylene, adhesive resin or compatibilizing material, and EVOH as the A, B, and C, respectively. The first composite stream thus created was manipulated in a series of ISG's to form a second composite stream, with both Ross ISG's and those of the type shown in Fig. 3, respectively, being employed in various runs. The second composite stream was then passed through a symmetricizer as in Fig. 5A-C and molded in the apparatus of Figures 10A-C by dropping a "gob" on the retracted piston X (Fig. 10A), lowering mold core Y (Fig. 10B), and then raising piston X to simulate injection molding (Fig. 10C).

The cans of 32 and 42 mil sidewall thicknesses thus formed were subjected to a number of tests, and the number and type of ISG's used, and the amounts of EVOH and compatibilizing material used were varied in different runs to quantify the effect of these variations on the performance characteristics of the cans.

The following basic measurements were undertaken:

30

A. Oxygen Barrier Measurements - The molded cans were double seamed with aluminum lids and sealed with epoxy. Oxygen permeabilities were measured at 23°C and 60 percent relative humidity on Modern Control's

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Oxtran 1050™ permeability tester. An average of three cans was tested for each condition or each run.

5       B. Xylene Permeability Measurements - The cans were filled with xylene, double seamed with aluminum  
placed inside a catch tray in an adequately vented hood,  
and weighed as a function of time at regular intervals  
over a period of 20 days to monitor the rate of loss of  
10       xylene at ambient temperature. An average of two cans was tested for each condition.

15       C. Microscopic Verification of Lamellar Morphology - For verification of the lamellar morphology in the can walls similar to that undertaken in previous  
examples, low voltage SEM microscopy was used. Sidewall  
cross-sections of the can near the bottom, in the middle  
and near the lip were examined in both the axial and  
hoop directions.

20       D. Environmental Stress Crack Resistance - To assess their resistance to environmentally induced failures, the molded barrier containers associated with each run were evaluated according to ASTM D2561-84. The  
25       molded cans were filled with 10 percent Igepal® C0630 detergent solution produced by GAF Corporation and double seamed with aluminum lids. Each container was placed in a separate reclosable plastic storage bag and placed in the hood at room temperature. The containers  
30       were inspected at regular intervals of time for evidence of cracks or leakage of the contents thereof, with the time to observation of the failure of a container being recorded. A minimum of three containers were tested for any given run.

## Results of Testing and Discussion of Results

### A. Oxygen Barrier Characteristics

5 The barrier performance of the molded containers was investigated as a function of the total number of layers in the melt stream entering the formation or molding process, the amount of EVOH barrier resin, and the amount of compatibilizing material used.

10 Before proceeding further it should be noted as discussed in Example 1, that the can molding apparatus depicted in Fig. 10 produced flawed can bottoms which would interfere or which could interfere with the oxygen permeability measurements. Accordingly, to compensate  
15 for the flawed bottoms of the containers the oxygen permeability of the whole container was determined first as to each individual container. After a steady state was reached, the bottoms were epoxied and a new steady  
20 state transmission rate was recorded. This was undertaken to illustrate the effects of the flawed bottoms on the oxygen transmission data for these lamellar transfer molded containers.

#### a. The Effect of the Number of Layers in 25 the Stream to be Molded into a Desired Configuration

30 In order to evaluate the effect of barrier layer thickness on the oxygen transmission rate of the containers as a whole, the number of barrier layers and the total number of layers in the second composite stream was varied over a broad range by adding or removing ISG's of the type shown in Figure 3 and Ross ISG's.

Table 1 summarizes the results of varying barrier layer thickness on the oxygen permeability of the 32 mil thick sidewall containers. The data indicate a minimum in oxygen permeability when the number of layers in the second composite stream are within the range of 50 to 300. With relatively few layers in the stream, i.e., less than 50, the thicker barrier layers do not extend sufficiently in the mold cavity during the mold fill step to obtain adequate coverage along the entire length or cross-section of a container wall. With a large number of layers, the barrier layers are too thin and tend to become discontinuous. This has been confirmed by photomicrographs corresponding to having 1025 layers in the second composite stream, as compared to cross-sectional photomicrographs of articles molded from a second composite stream having 257 total layers. The tendency of the layers to become discontinuous causes the barrier performance of the container as a whole to eventually approach that of a conventional melt blend.

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Table 1. Effect of Number of Layers in Stream to Be Molded on Oxygen Transmission Rate of 32 Mil Wall Containers

5	Number of Barrier Layers	Total Number of Layers	Oxygen Transmission Rate (cc/day atm. pkg)	
			Whole Container	Bottom Epoxied
10	8	33	0.0075	0.0066
	16	65	0.0106	0.0050
	32	129	0.0068	0.0038
	64	257	0.0059	0.0046
	128	513	0.0166	0.0078
15	256	1025	0.0256	0.0238
	512	2049	0.0443	0.0386
	Melt Blend	---	0.5280	---
20	HDPE Control	---	0.3651	0.3060

25 The minimum in oxygen permeability in the 50 to 300 total layers range in the second composite stream amounts to approximately an 80-fold improvement in barrier performance as compared to an identically composed melt blend. The barrier level achieved in the containers of this example is equivalent to an oxygen ingress rate of less than 1.4 cubic centimeters in 12 months.

30 The oxygen permeability results as a function of the number of layers in the second composite stream for 42 mil thick sidewall containers are summarized in Table 2. The results indicate essentially the same trend in the dependence of the oxygen

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transmission rate of the cans on the number of layers in the second composite stream. In the 42 mil thick sidewall containers, below about 800 layers in the second composite stream, the barrier performance of the lamellar injection molded containers approaches that of a coextruded sheet with a perfectly uniform and continuous barrier layer in the structure.

Table 2. Effect of Number of Layers in the Stream to be Molded on Barrier Performance of 42 mil Wall Containers, HDPE/Plexar 2581 /Soarnol D

	Number of Barrier Layers	Total Number of Layers	Oxygen Transmission Rate (cc/day . atm . pkg)	
			Whole Container	Bottom Epoxied
15	16	65	0.0003	0.0003
	64	257	0.0007	0.0004
	256	1025	0.0012	---
20	1024	4097	0.0163	0.0096
	16384	65537	0.0640	0.0508
	Melt Blend	---	0.2755	0.2455

25

The barrier level of about 0.001 cubic centimeters per day per atmosphere per package achieved with these containers, which is the lowest barrier level which can be reliably reported given the measurement techniques used, is equivalent to an oxygen ingress rate of less than 1 cubic centimeter in a two year time period.

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b. The Effect of the Amount of EVOH Barrier Material in the Structure

Table 3 summarizes the oxygen permeability data for lamellar molded 42 mil thick sidewall cans with a varying amount of the EVOH barrier material incorporated within the containers. The total number of layers in the second composite stream which was molded was kept the same in each case at a total of 257 layers. The results indicate that at least 10 percent by weight of the particular EVOH material used is the minimum amount required to achieve the barrier levels of 0.001 cubic centimeters per day per atmosphere per package which were noted in Table 2.

Table 3. Effect of Amount of EVOH in Structure in Performance of 42 Mil Wall Containers, 257 layers total HDPE/Plexar 2581/Soarnol D

Amount of Soarnol D, wt. %	Oxygen Transmission Rate (cc/day . atm . pkg)	
	Whole Container	Bottom Epoxied
5	0.0062	---
10	0.0008	0.0005
15	0.0003	---

c. The Effect of the Amount of Plexar 2581™ Compatibilizing Material

Oxygen permeability measurements on containers having 257 total layers in the second composite stream and with 15 percent or 25 percent by weight of the Plexar 2581™ compatibilizing material showed no

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significant difference between the containers so constructed.

Given that a significant use of barrier resins is in food packaging and packaging materials, and given also that many consumers may prefer a pigmented or opaque packaging material, the effect on oxygen barrier performance of the addition of titanium dioxide pigment to 32 and 42 mil cans having 257 total layers was studied. The results show that the oxygen permeability characteristics of the 42 mil cans was not significantly affected by the addition of titanium dioxide while the 32 mil cans exhibited a noticeable loss of barrier due to larger titanium dioxide particles bursting through the thin layers of EVOH.

#### B. Xylene Permeation Characteristics

Many of the factors which were tested with regard to the oxygen permeability of cans molded from the high density polyethylene/Plexar/Soarnol D system were considered with regard to xylene permeation characteristics also, with the effect of the total number of layers on the xylene permeability of 32 mil can containers being summarized in Table 4. The data indicate a minimum in xylene permeability in the range of from about 50 to about 300 total layers in the second composite stream, which is similar to what was noted in the case of oxygen permeability. This minimum amounts to approximately a 160-fold improvement in barrier performance to xylene compared with a 32 mil high density polyethylene can. The melt blend apparently exhibits no real improvement over the high density polyethylene control. The barrier level which is achieved in the 32 mil cans is equivalent to a xylene

weight loss of less than .01 percent in 12 months. By comparison, there was virtually no loss of xylene to the atmosphere in a 20 day period from a 42 mil high density polyethylene/Soarnol D™ can.

5

Table 4. Effect of Number of Layers in Stream to be Molded on Xylene Permeation Rate of HDPE/Soarnol D 32 Mil Wall Containers

	<u>No. of Barrier Layers</u>	<u>Total No. of Layers</u>	<u>Wt Loss of Xylene mg/hr</u>
10	8	33	0.657
	16	65	0.371
	32	129	0.201
15	64	257	0.363
	128	513	0.461
	256	1025	1.811
	512	2049	2.791
20	Melt Blend	---	36.571
	HDPE Control	---	32.600

The addition of titanium dioxide pigment had a negligible effect on xylene permeability in this system for 42 mil thick cans molded from a second composite stream having 257 total layers.

#### C. Environmental Stress Crack Resistance

The cans which were tested showed no evidence of failure even after 240 hours at room temperature. Typically an acceptable environmental stress crack resistance for cans made from polyethylene, for example, is 120 hours.

Example 6

In this example multilayer cans were molded as in Example 5, but with a resin system including high density polyethylene having a melt index of 0.7 grams per 10 minutes and a density of 0.96 grams per cubic centimeter as the first material, Selar® PA3426 amorphous nylon having a reported density of 1.19 grams per cubic centimeter (commercially available from E. I. du Pont De Nemours and Company Inc. Wilmington, Delaware) as the second material, and the assignee's Primacor® 1410 coextrudable tie layer resin, having a melt index of 1.5 grams per 10 minutes and a density of 0.938 grams per cubic centimeter, as the third material.

The cans which resulted were subjected to xylene and oxygen barrier tests which are described in detail in Example 5. The xylene permeability results are summarized in Table 5, and show that the high density polyethylene/nylon/Primacor® 42 mil molded containers exhibit over a fifty-fold improvement in xylene permeability over a 42 mil high density polyethylene can at ambient temperatures. This improvement appears to be comparable with the permeability figures reported in United States Patent Nos. 4,410,482 to Subramanian, 4,416,942 to DiLuccio, and 4,444,817 to Subramanian for articles made by an extrusion blow molding process.

Table 5. - Xylene Permeability of HDPE/Amorphous Nylon Containers

5	<u>Structure</u>	<u>Avg. Weight Loss of Xylene</u>	
		<u>mg/hr</u>	<u>%/hr</u>
	HDPE	32.031	0.0109
10	HDPE (71% by volume)/Primacor 1410 (13%)/Sclar PA 3426 (16%)	0.607	0.0007

\*256 barrier layers (1025 total layers)

15           The oxygen permeability characteristics of the  
42 mil thick molded cans of this example are shown in  
Table 6. An eight-fold improvement in oxygen barrier  
performance over cans molded from high density  
polyethylene alone is evident. This figure is also  
20 similar to the improvement in oxygen barrier achieved  
with a high density polyethylene/Sclar® RB nylon laminar  
mixing process, as reported in Subramanian,  
"Permeability Barriers by Controlled Morphology of  
Polymer Blends," Polymer Engineering Science, Volume 25,  
25 No. 8, Mid June 1985.

Table 6. Oxygen Barrier Performance of  
HDPE/Amorphous Nylon Containers

5	<u>Structure</u>	<u>Oxygen Transmission Rate</u> <u>(cc/day. atm. package)</u>	
		<u>Whole</u> <u>Container</u>	<u>Bottom</u> <u>Epoxied</u>
	HDPE	---	0.1980
10	HDPE (71% by volume)/Primacor 1410 (13%)/Sclar PA 3426 (16%)	0.356	0.0254

\*256 barrier layers (1025 total layers)

#### 15 Example 7

20 This example used the apparatus and process of  
Examples 1 and 2 in exploring a system having poly-  
propylene as the structural component, rather than the  
HDPE previously studied, with the same EVOH as used in  
previous examples. Cans were molded in the 32 mil and  
42 mil wall thicknesses according to the procedures set  
forth in Example 1, and the barriers of these containers  
to oxygen and xylene were studied as a function of  
25 several variables.

30 With regard to oxygen barrier, the effects of  
the amount of EVOH barrier resin in the structure, and  
of the particular compatibilizing material used were  
studied.

#### a. Effect of Amount of EVOH Barrier Resin

Cans of the 42 mil wall thickness were  
molded for this test using a polypropylene characterized

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by a melt flow index of 12 and a density of 0.903 grams per cubic centimeter as a first material, Soarnol D® EVOH as a second material, and Admer QF-500 tie layer resin from Mitsui Petrochemicals Industries, Ltd. (an anhydride-grafted polypropylene with a melt flow rate (MFR) of 3 grams per 10 minutes and a density of 0.91 grams per cubic centimeter) as the third material at 25 percent by weight throughout.

The results of oxygen permeability testing conducted as in previous examples for the effect of various amounts of the EVOH barrier resin are shown in Table 7, and correspond to a barrier efficiency of about 50% relative to an ideally coextruded 1025 layer coextruded sheet. The lower barriers achieved were believed indicative of substantial layer break-up and discontinuities in the molded can walls. Scanning electron microscopy of sidewall cross-sections near the bottom, middle and top of the can in both the axial and hoop directions confirmed that such layer breakup was present.

25

30

Table 7. Effect of Amount of EVOH in Structure  
on Barrier Performance of PP/EVOH  
Containers

5	Amount of EVOH, Wt Percent	Oxygen Transmission Rate (cc/day. atm. package)	
		Whole Container	Bottom Epoxied
	10	0.0117	0.0100
	15	0.0067	0.0022
10	20	---	0.0025

\*256 barrier layers (1025 total layers)  
PP and 25 wt % Admer QF500 tie layer resin

15                    b. Effect Of Compatibilizing Material

Though the Admer QF-500® tie layer resin exhibited strong interfacial adhesion in preliminary testing with the EVOH and polypropylene materials selected, with peel strengths in five-layer coextruded sheets of 5.2 pounds per inch and 7.5 pounds per inch in the machine and transfer directions, respectively, at the 5 percent level by weight, the molded cans delaminated easily with a gentle squeeze or in some cases only with the air ejection of the cans from the mold.

In an attempt to explore ways to improve the adhesion between the polypropylene and EVOH layers, other compatibilizing materials were evaluated. These were Admer QF-551 tie layer material from Mitsui (an anhydride-grafted polypropylene with an MFR of 5.7 and a density of 0.89) and Kraton® FG-1901X compatibilizing material from Shell Chemical Company, Houston, Texas (a functionalized triblock SEBS copolymer of a density of



0.91 grams per cubic centimeter). A comparison of oxygen permeation data for cans molded using the original Admer® QF-500 and the Kraton® FG-1901X materials shows the Admer® QF-500 tie layer material to be superior (see Table 8). In a comparison between the Admer® QF-500 and Admer® QF-551 tie layer resins, the latter resulted in better looking cans but no significant improvement in barrier or adhesion was observed.

It was also thought that increasing the melt temperature of the charged composite stream might increase the flow of the Admer® QF-500 compatibilizing material and improve adhesion. Increasing the temperature of the charged composite stream from 440°F-475°F showed no improvement in adhesion or barrier performance, however.

Table 8. Effect of Compatibilizing Material in Structure on Barrier Performance of 42 Mil PP/EVOH Containers

<u>Compatibilizing Material</u>	<u>Oxygen Transmission Rate (cc/day. atm. package)</u>	
	<u>Whole Container</u>	<u>Bottom Epoxied</u>
Admer™ QF500	0.0021	0.0017
Kraton™ G1901X	0.0351	0.0272

\*64 barrier layers (257 total layers)  
65% PP and 10 wt % Soarnol™ D EVOH

Some testing was also done of the containers and of the various materials and amounts thereof for xylene permeation resistance. The use of 10 percent

5 Soarnol D® EVOH resulted in a one hundred seventy-two-fold improvement in xylene permeation resistance over a polypropylene control. An additional 5 percent by weight of the Soarnol D® EVOH brought the improvement to

10 nearly a thousand-fold. (See Table 9)

Table 9. Effect of Amount of EVOH in Structure on Xylene Permeation of PP/EVOH Containers

15	Amount of SOARNOL™ D. EVOH (wt %)	Avg. Wt. Loss of Xylene mg/hr
	0	122.37
	10	0.709
20	15	0.127
	20	0.027

\*64 barrier layers (257 total layers)  
PP and 25 wt % Admer™ QF500 compatibilizing material

25

Where the barrier resin used was Eval® F resin (1.3 melt index, 1.19 grams per cubic centimeter density, Kuraray Company, Ltd.), the xylene permeation

30 rate through 32 mil thick wall containers molded from a 257 layer composite stream corresponded to 1.287 milligrams per hour of xylene weight loss. This figure represents nearly a hundred-fold improvement in xylene barrier over a polypropylene control, as compared to a

one hundred seventy-two-fold improvement with 10 percent Soarnol D® EVOH.

Example 8

5           In this example and in Examples 9 and 10, the effects of a lamellar construction are explored in terms of the environmental stress crack resistance(ESCR), deflection temperature under load(DTUL), and heat sag of various structural systems. In this and subsequent  
10 examples where performed, the environmental stress crack resistance for a test specimen was determined according to ASTM D1693 with synthetic gasoline (75 weight percent isooctane and 25 weight percent toluene) at 2000 psi  
15 constant applied stress. The distortion temperature under load for unannealed and annealed specimens was determined according to ASTM D648, and the heat sag after a specimen had been exposed to a temperature of 250 degrees Fahrenheit for a period of an hour.

20           This example looks primarily at systems of polycarbonate/polybutylene terephthalate (PBT) which are comprised of 15 parts and 30 parts of Celanex® 2002 PBT from Hoechst Celanese with the remaining 85 and 70  
25 parts, respectively, comprising the assignee's Calibre® 300-10 polycarbonate. The Celanex™ 2002 material possessed a reported density of 1.31 grams per cubic centimeter (with no melt index provided by the manufacturer), while the assignee's polycarbonate  
30 material had a melt index of 10 grams per 10 minutes and a density of 1.2 grams per cubic centimeter.

Test specimens were for one set of tests molded using the same equipment, except for the substitution of a four cavity test specimen mold as detailed earlier,

and according to the same general procedures used in previous Examples from layered composite streams having 33, 65, 129, 257, 513 and 1,025 total layers, and from a melt blend both by transfer and injection molding. Test results from the first set of tests for the basic 85/15 system are reported in Table 10, while the results for the basic 70/30 system are shown in Table 11. The results obtained for a polycarbonate/toughened-PBT system are provided in Table 12. Based on additional tests conducted to determine the effect of a lamellar construction on other structural properties, no loss in other structural properties was seen for any of the specimens thus made and otherwise tested compared to specimens formed from a melt blend of the same materials.

Table 10. Lamellar Molded PC/PBT (85/15) Specimens  
Effect of Number of Layers in Stream to be Molded

<u>No. of Layers</u>	<u>ESCR(min.)</u>	<u>DTUL</u> <u>Unannealed/Annealed</u> <u>(°C/°C)</u>		<u>Heat Sag</u> <u>(mm)</u>
		<u>@ 66 psi</u>	<u>@ 264 psi</u>	
33	94.3±42.9	140.4/151.6	118.1/149.4	1.8±1.4
65	81.3±12.3	140.5/150.1	125.0/147.6	3.4±0.3
129	51.0±4.6	137.8/148.0	120.2/146.0	2.5±0.3
257	68.3±8.1	135.3/150.6	121.8/146.4	2.5±1.1
513	64.0±10.5	135.6/146.5	116.6/142.0	2.7±1.1
1025	52.0±4.6	133.0/145.7	116.5/140.8	3.2±1.3
Melt Blend, Injection Molded	15.0±0.1			
Melt Blend, Transfer Molded	14.7±2.1	116.5/125	104.9/120.0	34.7±

25

30

Table 11. Lamellar Molded PC/PBT (70/30) Specimens  
Effect of Number of Layers in Stream to be Molded

<u>No. of Layers</u>	<u>ESCR(min.)</u>	<u>DTUL Unannealed/Annealed (°C/°C)</u>		<u>Heat Sag(mm)</u>
		<u>@ 66psi</u>	<u>@ 264psi</u>	
33	203.7±22.5	139.1/151.6	119.2/149.3	3.4±0.7
65	193.5±20.5	138.7/149.5	118.2/147.0	5.5±0.9
129	167.7±36.2	136.8/147.6	116.0/143.7	3.9±0.3
257	198.7±22.0	133.7/150.2	109.5/145.3	3.8±1.7
513	210.3±101	133.4/146.1	120.2/141.8	2.8±1.0
1025	153.5±27.6	133.2/144.7	111.6/139.5	3.5±0.4
Melt Blend, Transfer Molded	176.0±58.0	116.9/125.4	101.2/120.2	33.1±0.1

20Table 12. Lamellar Molded PC/PBT (85/15) (Toughened)  
Specimens. Effect of Number of Layers in  
Stream to be Molded

<u>No. of Layers</u>	<u>DTUL Unannealed/Annealed (°C/°C)</u>	
	<u>@ 66 psi</u>	<u>@ 264 psi</u>
25		
65	135.4/148.2	116.0/144.8
257	133.0/147.3	120.0/143.2
Melt Blend, Transfer Molded	116.0/123.3	106.8/118.4
30 Melt Blend, Injection Molded	114.9/122.4	103.7/117.8

Test specimens were also prepared on the same equipment and having the same number of layers but at three different proportions of the materials to examine

the effect of composition changes on the DTUL and ESCR of the specimens. The results from these tests are reported in Table 13, and again, no loss in other structural properties was seen for specimens made and tested as indicated.

5  
Table 13. Effect of Composition (129 layers)

Amount of PBT <u>(wt %)</u>	<u>ESCR(min.)</u>	DTUL		Heat <u>Sag(mm)</u>
		Unannealed/Annealed <u>(°C/°C)</u>		
		<u>@ 66 psi</u>	<u>@ 264 psi</u>	
15	51.0±4.6	137.8/148.0	120.2/146.0	2.5±0.3
30	167.7±36.2	136.8/147.6	116.0/143.7	3.9±0.3
50	>5700	133.9/146.6	102.0/140.4	--

#### Example 9

20           This example looks at the benefits accruing  
from a lamellar construction in terms of the  
environmental stress crack resistance and deflection  
temperature under load of systems having 15 and 30 parts  
of Celanex® 2002 PBT by weight and 85 and 70 parts,  
25   respectively, of a 65 to 35 part polycarbonate/ABS  
blend, as a function of the total number of layers  
formed in the composite stream to be molded. The blend  
had a melt index of 3 grams per 10 minutes (230°C/3.8  
kg) and a density of 1.12 grams per cubic centimeter,  
30   while the PBT had the properties ascribed to the Hoechst  
Celanese material previously. Test members were molded  
as in Example 8, with the same maintenance of other  
physical or structural properties seen in Example 8.  
The ESCR and DTUL results are reported in Tables 14 and  
15 below, respectively, for the 85/15 and 70/30 systems.

Table 14. Effect of Number of Layers in Stream to be Molded  
- PC/ABS Blend/PBT (85/15)

<u>No. of Layers</u>	<u>ESCR(min.)</u>	DTUL		Heat Sag (mm)
		Unannealed/Annealed (°C/°C)		
		@ 66 psi	@ 264 psi	
33	56.7±25.0	123.6/137.5	93.8/127.9	11.6±0.7
65	86.3±32.5	124.1/128.0	99.8/115.2	10.0±1.1
129	58.7±12.7	125.0/137.5	96.2/132.3	10.3±
257	30.7±8.3	122.8/135.9	95.3/124.3	21.9±1.5
513	53.7±6.4	120.2/132.5	92.9/122.2	16.7±2.1
1025	34.0±4.4	118.1/130.9	89.0/120.7	23.9±1.0
Melt Blend, Transfer Molded	8.7±0.6	96.1/105.6	86.6/102.1	125.6±
Melt Blend, Injection Molded	12.0±3.0	95/106	86/99	-

Table 15. Effect of Number of Layers in Stream to be Molded  
- PC/ABS Blend/PBT (70/30)

<u>No. of Layers</u>	<u>ESCR(min.)</u>	DTUL		Heat Sag (mm)
		Unannealed/Annealed (°C/°C)		
		<u>@ 66 psi</u>	<u>@ 264 psi</u>	
33	95.7±24.0	123.3/137.6	96.1/130.1	8.3±2.7
65	121.7±23.4	124.7/137.3	97.1/129.2	7.8±4.7
129	107.0±8.7	123.9/136.4	98.3/128.6	11.0±3.0
257	93.0±31.0	119.1/131.9	92.2/120.0	15.2±3.2
513	117.3±22.8	118.1/131.2	87.3/122.4	12.6±1.3
1025	100.0±14.9	113.3/128.4	86.0/115.7	16.4±2.0
Melt Blend, Transfer Molded	64.0±10.5	92.8/103.4	75.6/97.4	80.1±1.4
Melt Blend, Injection Molded	13.7±1.2	89/101	73/92	-



Example 10

This example explores the environmental stress crack resistance and deflection temperature under load of test articles molded from composite streams having various numbers of layers of the assignee's Calibre® 300-10 polycarbonate (melt index of 10 grams per 10 minutes; density of 1.2 grams per cubic centimeter) and Traytuf® 1006-C polyethylene terephthalate (PET) from The Goodyear Tire and Rubber Company (melt index not reported; density of 1.37 grams per cubic centimeter), in systems comprising 30 parts PET with 70 parts polycarbonate by weight, and 15 parts PET with 85 parts polycarbonate by weight. The molding and testing procedures and equipment were those used in Examples 8 and 9 above. Test results are reported in Tables 16 and 17, and again no loss of other structural properties was observed compared to a melt blend of the materials in these systems.

Table 16. Effect of Number of Layers in Stream to be Molded  
- PC/PET (85/15)

<u>No. of Layers</u>	<u>ESCR(min.)</u>	<u>DTUL</u>		<u>Heat Sag (mm)</u>
		<u>Unannealed/Annealed</u>		
		<u>(°C/°C)</u>		
		<u>@ 66 psi</u>	<u>@ 264 psi</u>	
65	24.3±5.9	137.5/147.8	111.4/145.5	4.5±0.4
129	24.3±0.6	136.2/148.7	113.2/146.0	3.4±0.6
257	25.0±6.2	134.6/147.6	112.0/145.3	5.3±1.2
513	25.0±5.2	138.0/148.1	108.7/145.8	5.6±0.4
1025	26.0±3.5	137.5/148.2	109.6/145.6	4.8±0.3
Melt Blend, Transfer Molded	11.3±1.5	131.7/144.3	107.4/141.5	4.5±0.3

Table 17. Effect of Number of Layers in Stream to be Molded  
- PC/PET (70/30)

<u>No. of Layers</u>	<u>ESCR(min)</u>	<u>DTUL</u> <u>Unannealed/Annealed</u> <u>(°C/°C)</u>		<u>Heat Sag</u> <u>(mm)</u>
		<u>@ 66 psi</u>	<u>@ 264 psi</u>	
65	23.0±2.0	133.4/147.4	97.8/144.6	6.0±0.4
129	32.3±5.1	135.5/148.5	100.3/145.9	4.2±0.9
257	22.0±1.7	136.2/147.8	97.5/145.5	7.0±1.0
513	34.3±1.5	135.7/148.7	101.4/146.6	5.5±0.4
1025	26.0±1.0	133.3/147.5	100.7/144.2	7.2±0.8
Melt Blend, Transfer Molded	19.3±4.0	125.4/142.6	97.2/139.7	5.8±0.4

15           The foregoing examples demonstrate that the processes and apparatus of the present invention are well suited for overcoming the deficiencies of the known art.

20           Large improvements in barrier to gases and solvents and in environmental stress crack resistance, and additional improvements in distortion temperature under load, are seen to result from such a lamellar construction compared to articles comprised of a melt  
25 blend of the same materials in the same proportions.

30           Similar improvements in filled systems with respect to the control of the coefficient of linear thermal expansion of an article, in the shielding of electromagnetic interference, and in ignition resistance should also be available by the lamellar constructions made possible by the present invention.

## WHAT IS CLAIMED IS:

1. A process for making a moldable multilayer plastic article, comprising the steps of:

5 coextruding discrete, generally planar layers of first and second diverse thermoplastic resinous materials in a first composite stream; and

forming the first composite stream into a desired configuration by some process other than thermoforming.

10 2. A process as defined in Claim 1, wherein the first composite stream is formed into a desired configuration by injection molding, transfer molding, compression molding, injection blow molding, extrusion  
15 blow molding, or displacement blow molding.

3. A process as defined in Claims 1 or 2, wherein the first composite stream is formed into a desired configuration having at least one critical  
20 surface such that a plurality of layers of the first and second materials lie generally parallel to such surface.

4. A process as defined in Claims 1 or 2, wherein the first composite stream is injected into a

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plurality of mold cavities as part of a multicavity injection molding process.

5. A process for making a moldable multilayer plastic article, comprising the steps of:

- 5           coextruding discrete, generally planar layers of first and second diverse thermoplastic resinous materials in a first composite stream;
- manipulating the first composite stream to form
- 10   a second composite stream having an increased number of discrete, generally planar layers of the first and second diverse thermoplastic materials compared to the first composite stream; and
- 15           forming the second composite stream into a desired configuration by some process other than thermoforming.

6. A process as defined in Claim 5, wherein
- 20   the second composite stream is formed into a desired configuration by injection molding, transfer molding, compression molding, injection blow molding, extrusion blow molding, or displacement blow molding.

- 25           7. A process as defined in Claims 5 or 6, wherein the step of manipulating the first composite stream to form the second composite stream includes:

- dividing the first composite stream to form a
- 30   plurality of substreams collectively containing an increased number of discrete, generally planar layers of the first and second materials compared to the first composite stream; and

stacking the plurality of substreams.

8. A process as defined in Claim 7, wherein the dividing and stacking steps are accomplished by passing the first composite stream through one or more interfacial surface generators.

5

9. A process as defined in Claims 5 or 6, wherein the second composite stream is formed into a desired configuration having at least one critical surface such that a plurality of layers of the first and second materials lie generally parallel to such surface.

10

10. A process as defined in Claims 5 or 6, wherein the second composite stream is injected into a plurality of mold cavities as part of a multicavity injection molding process.

15

11. A process as defined in Claims 4 or 10, wherein the mold cavities possess differing geometries.

20

12. A process as defined in Claims 4, 10 or 11, wherein at least one of the first and second materials comprises less than 15 percent by volume of the injected stream.

25

13. A process as defined in Claim 12, wherein layers of the at least one material extend fully throughout the plurality of mold cavities and the multilayer articles produced therefrom.

30

14. A process as defined in Claims 3 or 9, wherein no more than 10 percent of the layers of the first and second materials adjacent the critical surface have an interfacial surface area to unit thickness ratio of less than 10 to 1.

15. A process as defined in Claims 3 or 9, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface are individually substantially uniformly thick.

5           16. A process as defined in Claims 3 or 9, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface have interfacial surface area to unit  
10 thickness ratios of at least 100 to 1.

          17. A process as defined in Claim 16, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical  
15 surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

          18. A process as defined in Claims 3 or 9, wherein the desired configuration possesses a uniformity  
20 of composition with respect to at least the first and second materials adjacent the critical surface.

          19. A process as defined in Claims 3 or 9, wherein the layers of the first and second materials  
25 lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

          20. A process for making a moldable multilayer  
30 plastic article, comprising the steps of:

          coextruding discrete, generally planar layers of first, second and third diverse thermoplastic materials in a selected layer order in a first composite stream, the selected layer order being characterized by

the placement of a layer of the third material between any otherwise adjacent layers of the first and second materials; and

5 forming the first composite stream into a desired configuration by some process other than thermoforming.

21. A process as defined in Claim 20, wherein the first composite stream is formed into a desired configuration by injection molding, transfer molding, 10 compression molding, injection blow molding, extrusion blow molding, or displacement blow molding.

22. A process as defined in Claims 20 or 21, wherein the first composite stream is formed into a 15 desired configuration having at least one critical surface such that a plurality of layers of the first, second and third materials lie generally parallel to such surface in said selected layer order.

20 23. A process as defined in Claims 20 or 21, wherein the first composite stream is injected into a plurality of mold cavities as part of a multicavity injection molding process.

25 24. A process for making a moldable multilayer plastic article, comprising the steps of:

30 coextruding discrete, generally planar layers of first, second and third diverse thermoplastic resinous materials in a selected layer order in a first composite stream, the selected layer order being characterized by the placement of a layer of the third

material between any otherwise adjacent layers of the first and second materials;

manipulating the first composite stream to form a second composite stream having an increased number of discrete, generally planar layers of the first and second diverse thermoplastic materials compared to the first composite stream; and

forming the second composite stream into a desired configuration by some process other than thermoforming.

25. A process as defined in Claim 24, wherein the second composite stream is formed into a desired configuration by injection molding, transfer molding, compression molding, injection blow molding, extrusion blow molding, or displacement blow molding.

26. A process as defined in Claims 24 or 25, wherein the step of manipulating the first composite stream to form the second composite stream includes:

dividing the first composite stream to form a plurality of substreams collectively containing an increased number of discrete, generally planar layers of the first, second and third materials compared to the first composite stream; and

stacking the plurality of substreams.

27. A process as defined in Claim 26, wherein the dividing and stacking steps are accomplished by passing the first composite stream through one or more interfacial surface generators.



28. A process as defined in Claims 24 or 25,  
wherein the second composite stream is formed into a  
desired configuration having at least one critical  
surface such that a plurality of layers of the first,  
second and third materials lie generally parallel to  
5 such surface in said selected layer order.

29. A process as defined in Claims 24 or 25,  
wherein the second composite stream is injected into a  
plurality of mold cavities as part of a multicavity  
10 injection molding process.

30. A process as defined in Claims 23 or 29,  
wherein the mold cavities possess differing geometries.

31. A process as defined in Claims 23, 29 or  
15 30, wherein at least one of the first, second and third  
materials comprises less than 15 percent by volume of  
the injected stream.

32. A process as defined in Claim 31, wherein  
20 layers of the at least one material extend fully  
throughout the plurality of mold cavities and the  
multilayer articles produced therefrom.

33. A process as defined in Claims 22 or 28,  
25 wherein no more than 10 percent of the layers of the  
first, second and third materials adjacent the critical  
surface have an interfacial surface area to unit  
thickness ratio of less than 10 to 1.

34. A process as defined in Claims 22 or 28,  
30 wherein at least the plurality of layers of the first,  
second and third materials lying generally parallel to

the critical surface are individually substantially uniformly thick.

5 35. A process as defined in Claims 22 or 28, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 100 to 1.

10 36. A process as defined in Claim 35, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

15 37. A process as defined in Claims 22 or 28, wherein the desired configuration possesses a uniformity of composition with respect to at least the first, second and third materials adjacent the critical surface.

20 38. A process as defined in Claims 22 or 28, wherein the layers of the first, second and third materials lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

25

39. Apparatus for performing the process of any of Claims 1-38.

30 40. A multilayer plastic article made by the process of any of Claims 1-38.

41. An asymmetrical moldable multilayer plastic article comprising at least about 17 discrete layers of

a plurality of diverse thermoplastic resinous materials  
extending continuously throughout the article.

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## AMENDED CLAIMS

[received by the International Bureau on 22 May 1991 (22.05.91);  
original claims 11,12,14-16,18,19 amended; 30,31,33-35,37,  
38,39 and 40 other claims unchanged (4 pages)]

stacking the plurality of substreams.

8. A process as defined in Claim 7, wherein  
the dividing and stacking steps are accomplished by  
passing the first composite stream through one or more  
interfacial surface generators.

5

9. A process as defined in Claims 5 or 6,  
wherein the second composite stream is formed into a  
desired configuration having at least one critical  
surface such that a plurality of layers of the first and  
second materials lie generally parallel to such surface.

10

10. A process as defined in Claims 5 or 6,  
wherein the second composite stream is injected into a  
plurality of mold cavities as part of a multicavity  
injection molding process.

15

11. A process as defined in Claim 4, wherein  
the mold cavities possess differing geometries.

20

12. A process as defined in Claim 11, wherein  
at least one of the first and second materials comprises  
less than 15 percent by volume of the injected stream.

13. A process as defined in Claim 12, wherein  
layers of the at least one material extend fully  
throughout the plurality of mold cavities and the  
multilayer articles produced therefrom.

25

14. A process as defined in Claim 3, wherein no  
more than 10 percent of the layers of the first and  
second materials adjacent the critical surface have an  
interfacial surface area to unit thickness ratio of less  
than 10 to 1.

30

15. A process as defined in Claim 3, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface are individually substantially uniformly thick.

5 16. A process as defined in Claim 3, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 100 to 1.

10 17. A process as defined in Claim 16, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

15 18. A process as defined in Claim 3, wherein the desired configuration possesses a uniformity of composition with respect to at least the first and second materials adjacent the critical surface.

20 19. A process as defined in Claim 3, wherein the layers of the first and second materials lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

25 20. A process for making a moldable multilayer plastic article, comprising the steps of:

30 coextruding discrete, generally planar layers of first, second and third diverse thermoplastic materials in a selected layer order in a first composite stream, the selected layer order being characterized by the placement of a layer of the third material between

surface such that a plurality of layers of the first, second and third materials lie generally parallel to such surface in said selected layer order.

5 29. A process as defined in Claims 24 or 25, wherein the second composite stream is injected into a plurality of mold cavities as part of a multicavity injection molding process.

10 30. A process as defined in Claim 23, wherein the mold cavities possess differing geometries.

15 31. A process as defined in Claim 30, wherein at least one of the first, second and third materials comprises less than 15 percent by volume of the injected stream.

20 32. A process as defined in Claim 31, wherein layers of the at least one material extend fully throughout the plurality of mold cavities and the multilayer articles produced therefrom.

25 33. A process as defined in Claim 22, wherein no more than 10 percent of the layers of the first, second and third materials adjacent the critical surface have an interfacial surface area to unit thickness ratio of less than 10 to 1.

30 34. A process as defined in Claim 22, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to the critical surface are individually substantially uniformly thick.

35. A process as defined in Claim 22, wherein at least the plurality of layers of the first, second

and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 100 to 1.

5           36. A process as defined in Claim 35, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

10           37. A process as defined in Claim 22, wherein the desired configuration possesses a uniformity of composition with respect to at least the first, second and third materials adjacent the critical surface.

15           38. A process as defined in Claim 22, wherein the layers of the first, second and third materials lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

20           39. Apparatus for performing the process of any of Claims 1, 5, 20 or 24.

25           40. A multilayer plastic article made by the process of any of Claims 1, 15, 20 or 24.

30           41. An asymmetrical moldable multilayer plastic article comprising at least about 17 discrete layers of a plurality of diverse thermoplastic resinous materials extending continuously throughout the article.

FIG. 1

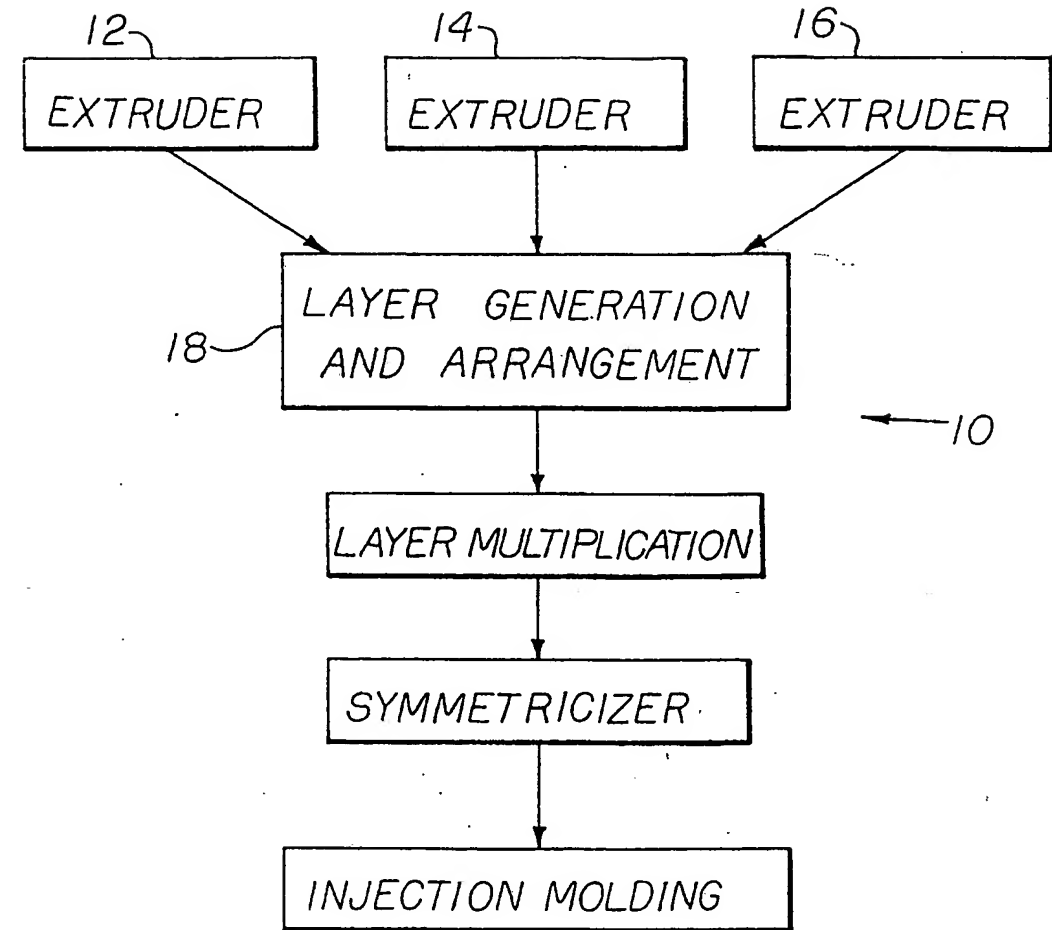
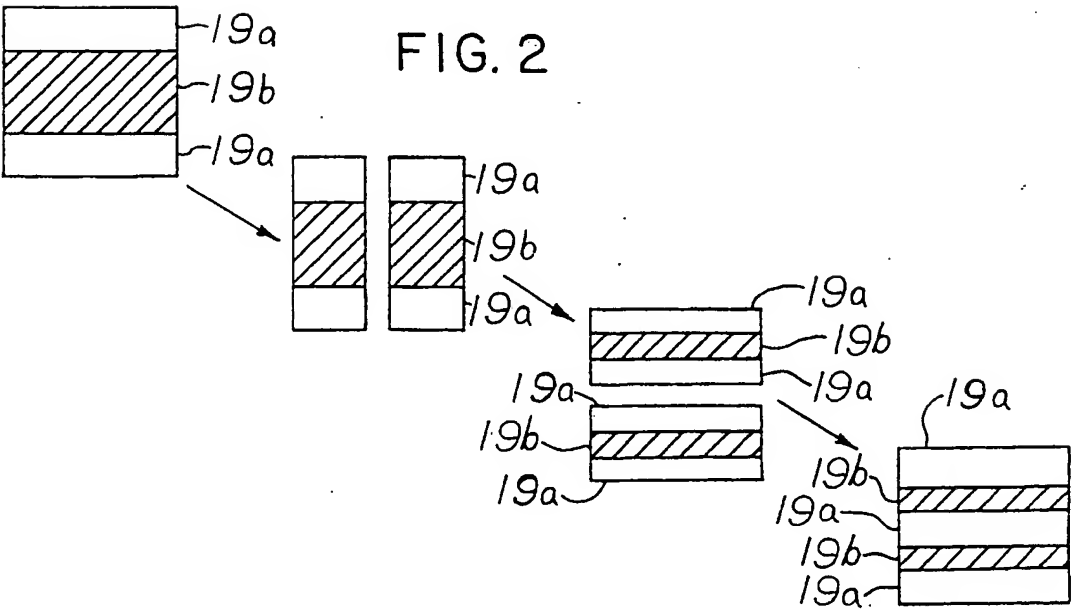


FIG. 2





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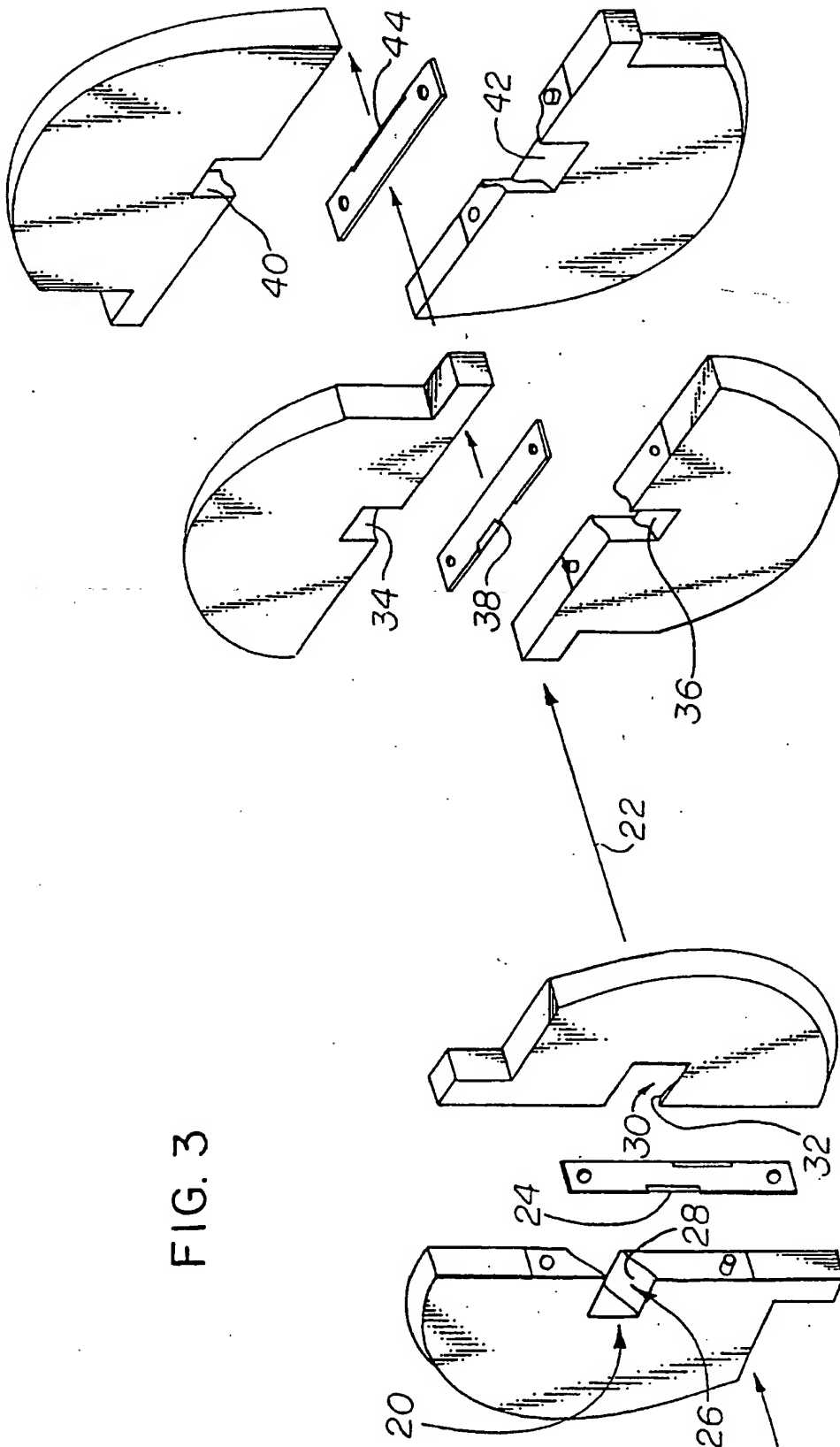


FIG. 3

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FIG. 4A



FIG. 4B



FIG. 4C

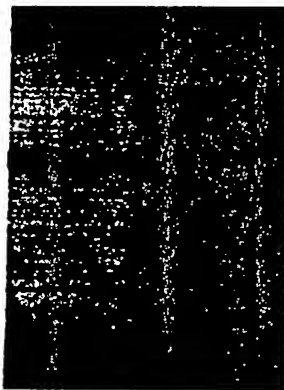


FIG. 4D



FIG. 4E



FIG. 4F



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FIG. 5A

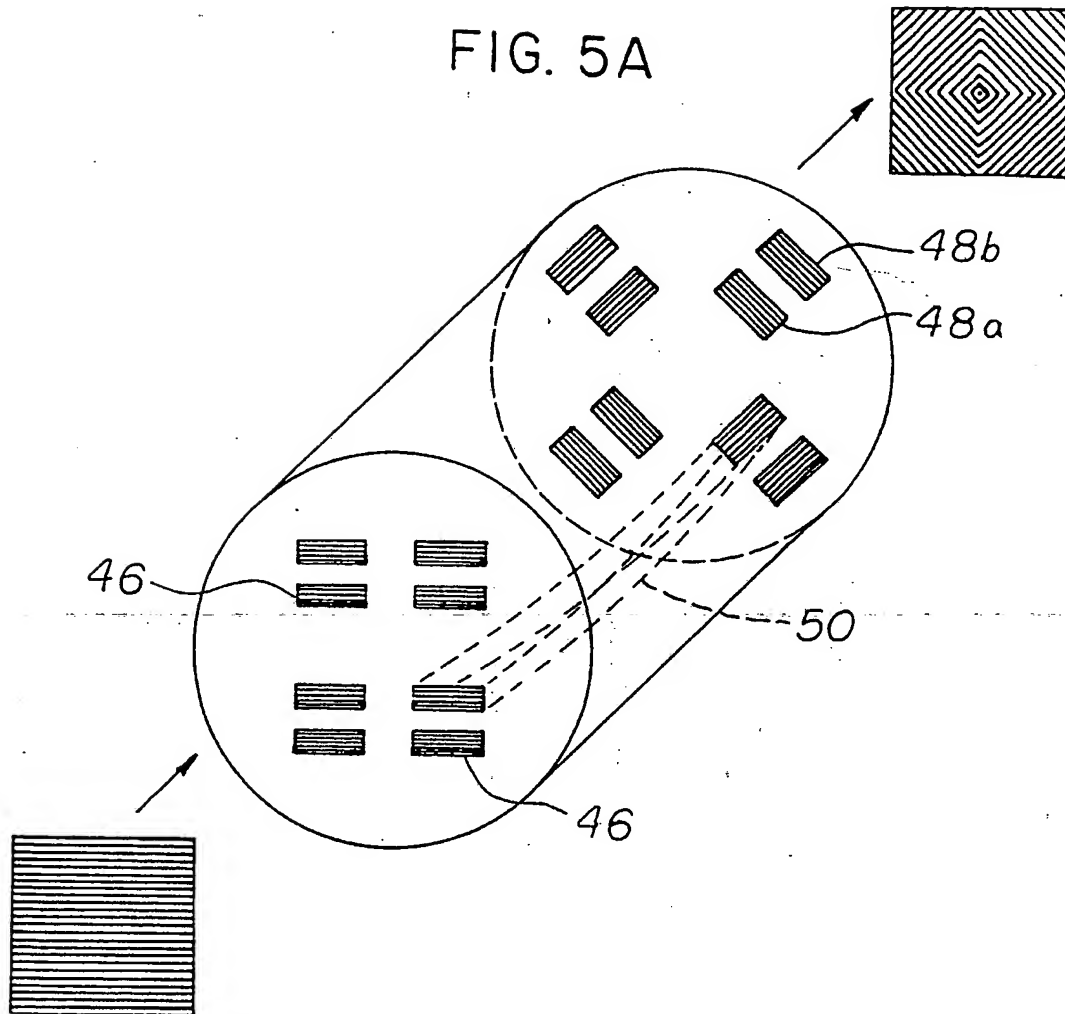


FIG. 5B

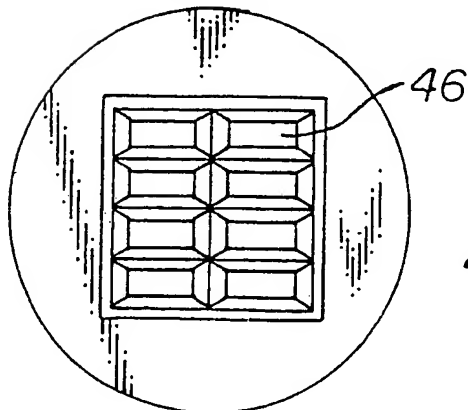
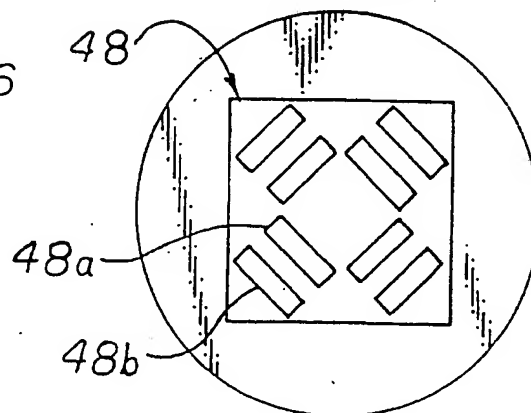


FIG. 5C



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FIG. 6A



FIG. 6B

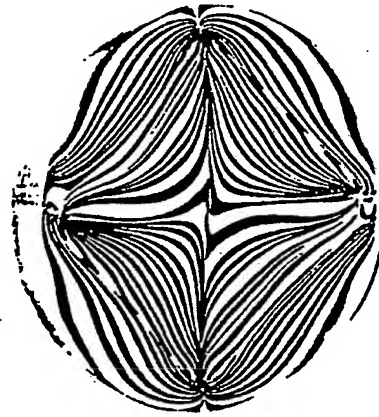
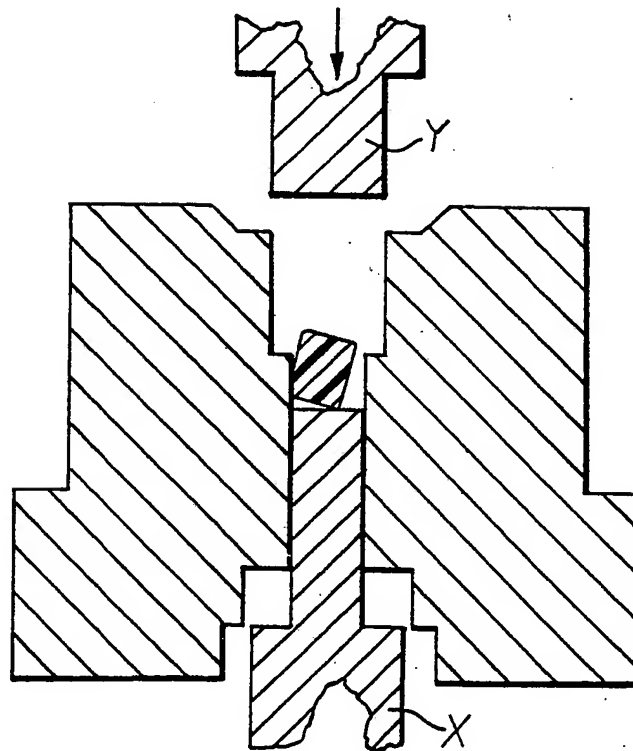


FIG. 10A



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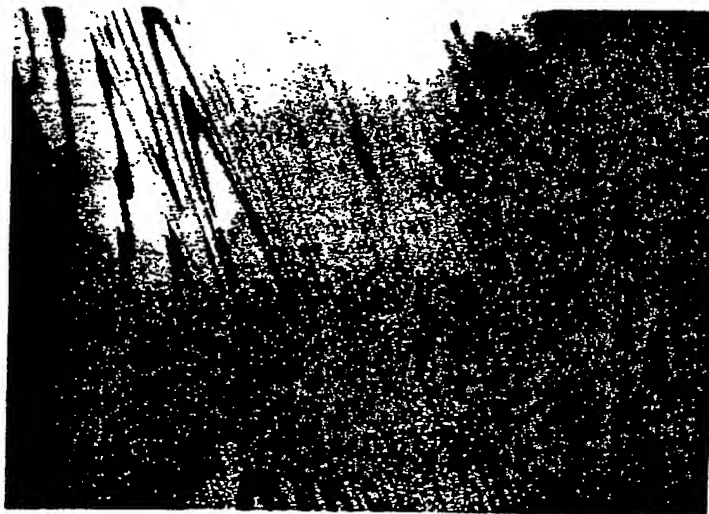


FIG. 7A



FIG. 7B

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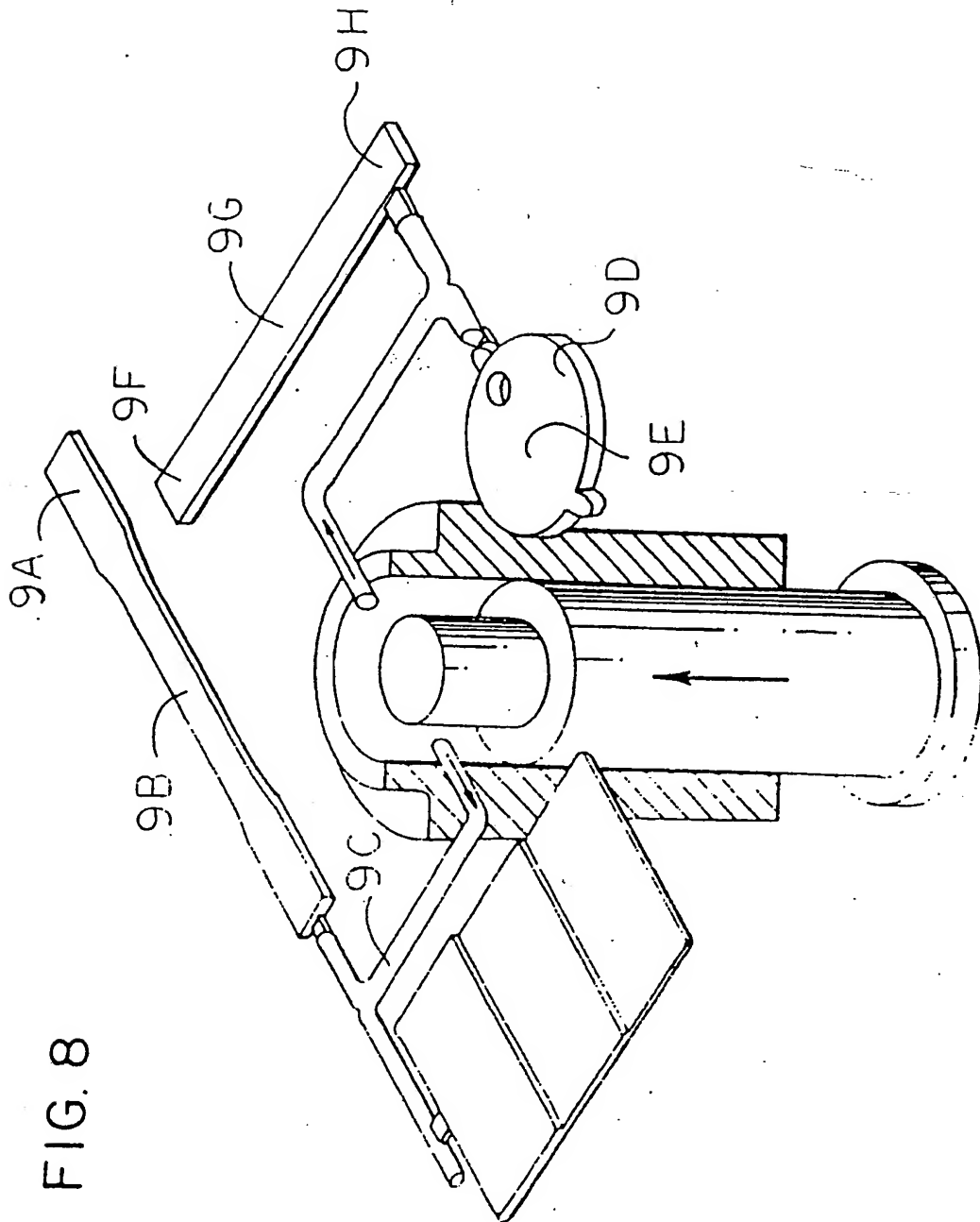


FIG. 8

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FIG.9C

FIG.9D

FIG.9E



FIG.9B

FIG.9H



FIG.9A

FIG.9F

FIG.9G

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FIG. 10B

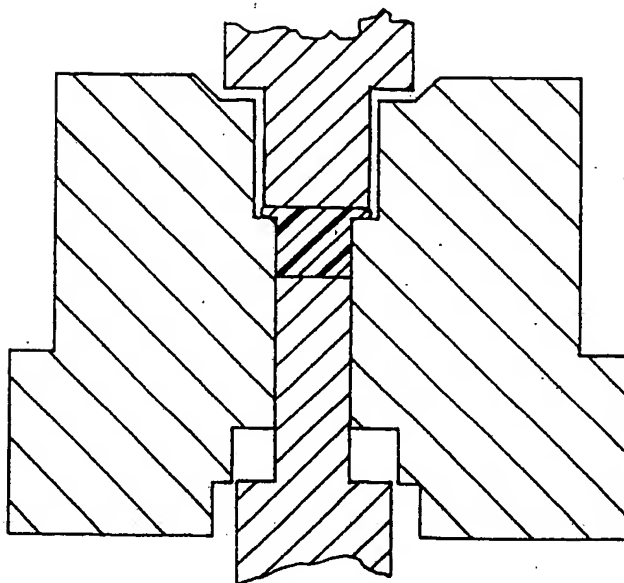
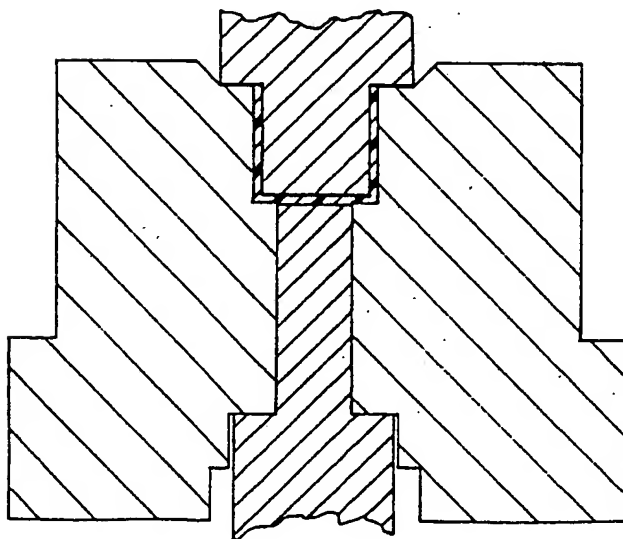


FIG. 10C





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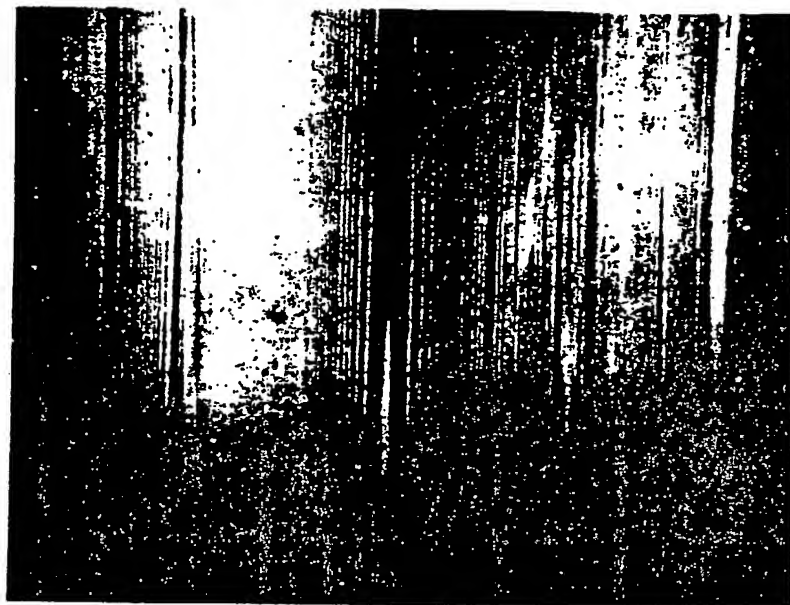


FIG. 11B

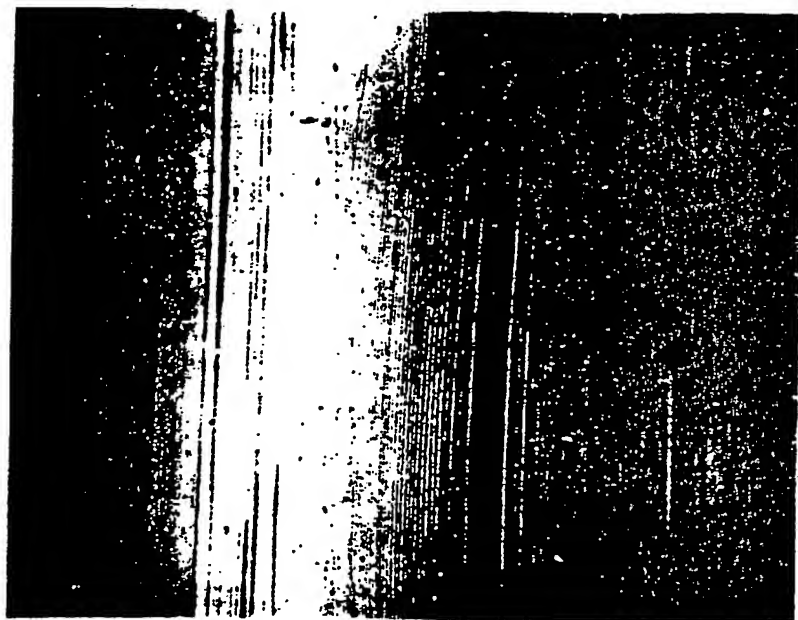


FIG. 11A

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/07327

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>1</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC B29C, 43/20, 45/02, 45/16, 49/04, 49/06, 49/22		
US 264/73, 75, 241, 245, 297.2, 328.8, 328.12, 510 425/130, 503, 588 428/98, 411.1, 35.7		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System <sup>1</sup>	Classification Symbols	
US	264/73, 75, 241, 245, 297.2, 328.8, 328.12, 510, 513, 514, 515 425/130, 132, 133.1, 133.5, 523, 588 428/98, 411.1, 35.7	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>6</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	US, A 3,716,612, Schrenk, 13 February 1973	1,2
Y	see figures and col. 1, lines 44-57, col. 2, lines 21-26, col. 10, line 42 to col. 11, line 23	4,20,21,23,41
X,E	US, A 4,978,493, Kersemakers 18 Dec 1990 (col. 2, lines 40-48; col. 4, line 58 to col. 5, line 35)	1,2,5,6,7,9,15, 18,19,20,21,24- 28, 34,37,38 4,10-13,23,29- 32,34,37,38
Y	US, A 3,239,197, Tollar 8 March 1966 (Figures, col. 2, lines 12-20, col. 3, lines 45-67, col. 5, lines 47-69)	1-38
Y	US, A 3,339,240, Corbett 5 September 1967 (Figure col. 1, lines 30-35, col. 1, lines 41-44 col. 4, lines 12-15, col. 3, lines 46-57)	4,10-13,23, 29-32,34,37,38
Y	JP, A, 59-091,042, Aisin Seikikk 17 November 1982 (Figure 5, Abstract)	4,10-13,23,29- 32,34,37,38,41
A	US, A 4,315,724 Taoka, 16 February 1982 (Figures)	1-41
<p><sup>19</sup> Special categories of cited documents: <sup>13</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>		Date of Mailing of this International Search Report <sup>3</sup>
08 March 1991		15 APR 1991
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
ISA/US		<i>Andie Robinson</i> Catherine Timm

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US,A, 3,557,265 Chisholm, 19 January 1971	1-41
A	US,A 3,565,985 Schrenk, 23 February 1971	1-41
A	US,A, 3,884,606, Schrenk, 20 May 1975	1-41
A	US,A 3,817,675, Maiacco, 18 June 1974	1-41

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_ because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claim numbers \_\_\_\_\_ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out<sup>1</sup>, specifically:
  
3. ☒ Claim numbers 39, 40 because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
  
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
  
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.